

A Study of the Conductivity and
Dissociation of Organic Acids in
Aqueous Solution Between Zero
and Thirty-Five Degrees

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

Baltimore

BY

EUGENE PINCKNEY WIGHTMAN

BALTIMORE

June, 1911

EASTON, PA.:
ESCHENBACH PRINTING CO.
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A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF ORGANIC ACIDS IN AQUEOUS SOLUTION BETWEEN ZERO AND THIRTY-FIVE DEGREES

HISTORICAL

White and Jones,¹ in their work on the conductivity and dissociation of organic acids in aqueous solution, give a survey of the data obtained up to that time, and a large amount of the earlier work is discussed in full. It is not necessary to repeat all of this discussion, but a short summary of the results as a whole will be given as an introduction to this work.

One of the first things noticed by early workers was the increase in molecular conductivity with rise in temperature and increasing dilution. It was shown also that this increase is, for most electrolytes in dilute solutions, a parabolic function of the temperature, and the following interpolation formula was deduced and employed by Euler:²

$$\lambda = a + bt - ct^2$$

in which λ is the molecular conductivity at the temperature t , a is the known conductivity at some other temperature, and b and c are constants depending upon the nature of the electrolytes. Extensive use has been made of this formula.

As the dilution increases the rate of increase in conductivity becomes less, and in some cases there is a maximum value of conductivity, as was shown by Grotian,³ Jahn,⁴ Schaller,⁵ and the later workers. As a matter of fact, the maximum occurs for nearly all strong electrolytes at dilutions at which the conductivity can be measured directly.

This is not the case with most of the organic acids, but indirect methods were devised by Ostwald⁶ and by White

¹ Am. Chem. J., **44**, 159 (1910).

² Z. physik. Chem., **21**, 257 (1896).

³ Pogg. Ann., **154**, 215 (1875).

⁴ Z. physik. Chem., **16**, 72 (1895).

⁵ *Ibid.*, **25**, 497 (1893).

⁶ *Ibid.*, **1**, 74, 97 (1887); **2**, 840 (1888).

and Jones,¹ based upon Kohlrausch's law of the independent migration velocities of ions, by means of which μ_{∞} for the acids could be determined.

Ostwald showed that there is a constant difference between μ_v for a given dilution, say thirty-second normal, of the sodium salt of any acid, and the μ_{∞} value of the same, which is found at about ten hundred and twenty-fourth normal. By means of this constant difference he calculated the μ_{∞} values of a large number of sodium salts without direct measurement, and from these it was easy to determine the μ_{∞} values of the acids in question, by subtracting the value for the migration velocity of the sodium ion, and adding the corresponding constant for hydrogen.

A second method suggested by Ostwald was based upon the fact that the velocities of anions of acids containing over twelve atoms in the anion are dependent upon the number of these atoms present—ions with the largest number of atoms having the smallest velocity.

The method of White and Jones (for monobasic acids) is based upon the direct measurement of the μ_{∞} value of the sodium salt of the acid and will be discussed later. The μ_{∞} values of the dibasic acids were determined by a graphic method similar to the second method used by Ostwald.

Just as the molecular conductivity increases at a diminishing rate with dilution, so also it increases at a diminishing rate with rise in temperature, as was brought out by Schaller² and by Noyes.³

Another important fact is the decrease in dissociation with rise in temperature, first noticed by Arrhenius⁴ in the case of phosphoric and hypophosphoric acids, later brought out by Schaller⁵ and a number of others,⁶ and finally thoroughly

¹ Am. Chem. J., **44**, 159 (1910).

² Z. physik. Chem., **25**, 497 (1898).

³ J. Am. Chem. Soc., **26**, 134 (1904); **30**, 335 (1908); **31**, 987 (1909).

⁴ Z. physik. Chem., **4**, 96 (1889).

⁵ *Ibid.*, **25**, 497 (1898).

⁶ Jones and West: Am. Chem. J., **34**, 357 (1905); Jones and Jacobson: *Ibid.*, **40**, 355 (1908); Jones and Clover; *Ibid.*, **43**, 187 (1910); White and Jones: *Ibid.*, **44**, 159 (1910).

established by the work of Noyes¹ at higher temperatures. No entirely satisfactory explanation of this decrease in dissociation has been given; but the results of Noyes in his first work² show that the dissociations of the two salts, sodium chloride and potassium chloride, are nearly identical at all temperatures and concentrations; and he says: "This gives support to the idea that decrease of conductivity and of calculated dissociation with rise in temperature is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity." More will be said about this in another connection.

It was pointed out by the later workers (Schaller³ was one of the first) that the temperature coefficients of conductivity increase with dilution and decrease with rise in temperature for acids, and increase with temperature for neutral salts. Amino acids are an exception to this, as was shown by White and Jones.⁴ They explain the increase with rise in temperature as "probably due to the formation of inner salts having both acidic and basic groups, which break up with rise in temperature." The decrease of the temperature coefficients for nearly all other acids is explained by them in terms of the theory of hydration.⁵

It was found by White and Jones that the Ostwald dilution law⁶ holds very well for dilute, weak organic acids, with the exception of the amino acids. The law is expressed thus:

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

where $\alpha = \frac{\mu_v}{\mu_\infty}$ is the dissociation, V is the volume, and K is a constant. The law is easily deduced from the gas laws and those of osmotic pressure. The discrepancies in the temperature coefficients in the case of amino acids were explained as stated above, viz., as due to the breaking down of the inner salts.

¹ J. Am. Chem. Soc., **26**, 134 (1904); **30**, 355 (1908); **31**, 987 (1909).

² *Ibid.*, **26**, 134 (1904).

³ Z. physik. Chem., **25**, 497 (1898).

⁴ Am. Chem. J., **44**, 159 (1910).

⁵ *Ibid.*, **40**, 402 (1908).

⁶ Z. physik. Chem., **2**, 36 (1888); **3**, 170 (1889). Jahn: *Ibid.*, **23**, 545 (1900).

Strong acids (and also other strong electrolytes) do not conform to the Ostwald law, and a large number of empirical formulae have been suggested,¹ all of which hold fairly well for specific cases, but only a few of which are of general application. These are discussed very thoroughly by Noyes,² who says of the following formulae:

$$\frac{\Delta_0 - \Delta}{C^{1/3}} = K \text{ (Kohlrausch)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{1/3} C^{1/3}} = K \text{ (Barmwater)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{3/2} C^{1/2}} = K \text{ (Van't Hoff)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^2 C^{1/2}} = K \text{ (Rudolphi)}$$

"The Kohlrausch formula expresses the results for both salts (potassium and sodium chlorides) at all temperatures without great error, and the same is true of the Barmwater formula except at the highest temperature, where the deviation with both salts is large. The van't Hoff and Rudolphi formulas do not accord at all with the observed values at 306°, the deviations in the case of the latter being especially large; while at the lower temperatures, 140°, 218° and 281°, the van't Hoff formula is far less satisfactory than those of Kohlrausch and Barmwater. On the whole, therefore, the simple Kohlrausch formula furnishes the best representation of the results and the Barmwater next best."

In terms of the Ostwald formula, i. e., using the same notation, these would be:

$$\frac{1 - \alpha}{\sqrt[3]{I/V}} = K \text{ (Kohlrausch)}$$

$$\frac{1 - \alpha}{\sqrt[3]{\alpha/V}} = K \text{ (Barmwater)}$$

¹ Wied Ann., **26**, 200 (1885); **50**, 394 (1893). MacGregory: *Ibid.*, **51**, 133 (1894). Barmwater: *Z. physik. Chem.*, **28**, 134, 428 (1899). Sabat: *Ibid.*, **41**, 224 (1902). Müller: *Compt. rend.*, **123**, 505 (1899). Kohlrausch: *Sitz. preus. Akad.*, **44**, 1002 (1900). Rudolphi: *Z. physik. Chem.*, **17**, 385 (1895). Van't Hoff: *Ibid.*, **18**, 300 (1895). Kohlrausch: *Ibid.*, **18**, 662 (1895). Storch: *Ibid.*, **19**, 13 (1896). Bancroft: *Ibid.*, **31**, 188 (1899). Jahn: *Ibid.*, **37**, 499 (1901); **41**, 265, 288 (1902). Nernst: *Ibid.*, **38**, 493 (1901).

² J. Am. Chem. Soc., **26**, 162 (1904).

Noyes¹ says also, concerning strong electrolytes: "This principle has now received a further confirmation through the demonstration of the fact that certain purely empirical laws relating to the ionization of salts in water still continue to be valid, even when the physical condition of that solvent is greatly altered by a large change in the temperature. This principle is that the ionization of salts, strong acids and bases is a phenomenon primarily determined not by specific chemical affinities, but by electrical forces arising from charges on the ions; that it is not affected (except in a secondary degree) by chemical mass action, but is regulated by certain general, comparatively simple laws, fairly well established empirically but of unknown theoretical significance, and that, therefore, it is a phenomenon quite distinct in almost all its respects from the phenomenon of dissociation ordinarily exhibited by chemical substances, including that of the ionization of weak acids and bases."

He distinguishes between ordinary unchanged molecules, which he calls "chemical molecules," and a loosely united ionized molecule, or "electrical molecule."

Walden² in 1891 and 1892 showed, in his work on di-, tri-, and tetracarboxylic acids, that the general tendency of such organic acids is to dissociate, up to quite high dilutions, like monobasic acids. In the case of tribasic acids he mentions the three possibilities:



of which only the first takes place at ordinary dilutions.

The same thing was found to be the case by Walker,³ namely, that dibasic acids behave just like monobasic acids within the limits of dilutions at which he worked. Pimelic acid,

for instance, splits into H and $OOC(CH_2)_5COOH$, and not into H , H , and $OOC(CH_2)_5COO$.

¹ J. Am. Chem. Soc., **30**, 335 (1908).

² Z. physik. Chem., **8**, 434 (1891); **10**, 563 (1892).

³ J. Chem. Soc., **61**, 696 (1892).

EXPERIMENTAL

Apparatus

Burettes and flasks (200 cc., 250 cc., 500 cc., and 1000 cc.) were all calibrated by the method of Morse and Blalock¹ for a temperature of 20°. The 200 cc. flasks were also calibrated by weight, and the results were found to agree very closely. The time necessary to drain all pipettes and burettes was determined and properly taken into account in the measurements. The thermometers were also carefully standardized against a Reichsanstalt thermometer.

At first a Wheatstone bridge was used for making the conductivity measurements, and this was calibrated by the method of Strouhal and Barus.² Later a very fine Kohlrausch slide-wire bridge was obtained, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was five meters).

The resistance box employed in the later work was one that had been standardized by the U. S. Bureau of Standards. The one first used was later compared with this one, and was found to be accurate to well within the limits of experimental error.

Three thermostats were employed to keep the cells at constant temperature; one for 0°, similar to that described by Jones and Jacobson;³ one for 15° and 25°, a galvanized tub containing 25 or 30 liters of water, and in the bottom of which was placed a lead coil through which cold water was passed under constant pressure; a third for 35°, differing from the latter only in not having a coil in the bottom. They were both kept constantly stirred by propellers driven by a hot-air engine. In this way it was possible to keep the temperature constant to within 0°.02.

At first the thermostats were regulated by hand, and this was found to be sufficient, provided they were continually watched. It was found, however, that thermoregulators save both time and labor, so that finally these were installed.

¹ Am. Chem. J., **16**, 479.

² Wied. Ann., **10**, 326. Kohlrausch and Holborn: "Leitvermögen der Electrolyte," p. 45 (1898).

³ Am. Chem. J., **40**, 355 (1908).

They were of the general type used in this laboratory, so need not be described here.

The cells resembled those used by Jones and Bingham,¹ with platinum-plate electrodes, attached to glass tubes containing mercury, the tubes being sealed into ground-glass stoppers. As many as eight cells were employed with constants ranging from about 330 to about 10 in Siemens' units. A cell of special type,² having a very low constant, was used for obtaining the conductivity of the water.

In order to get a sharp reading in the cells, electrodes were covered with a fine coating of platinum black in the usual manner.

Mention only will be made of the viscosity apparatus, which was of the form used for such work in this laboratory,³ consisting of a picnometer, viscometer, and a stopwatch.

Reagents

Water for making up all solutions and for the final purification of the acids was obtained by the method of Jones and Mackay.⁴

Standard Acid.—Two methods were made use of for standardizing sulphuric acid; namely, the barium sulphate method, and a check method which consists in standardizing against a solution of sodium hydroxide, which, in turn, has been titrated against very thoroughly standardized hydrochloric acid. Both methods gave practically identical results.

As to the first one, the acid was made up to approximate strength (about 0.15 N) from pure concentrated sulphuric acid. Three 50 cc. portions of the dilute solution were then run into fairly large beakers and further diluted, and then heated nearly to boiling. A hot, dilute solution of barium chloride, containing a slight excess of the salt, was then poured gradually down the side of one of the beakers containing sulphuric acid, to which had been added a few drops of hydrochloric acid, and which was kept stirred all the while.

¹ Am. Chem. J., **34**, 493 (1905).

² *Ibid.*, **45**, 282 (1911).

³ Ostwald-Luther: Physik.-chem. Mess., 2nd Ed., p. 260. Z. physik. Chem., **61**, 651 (1908).

⁴ Am. Chem. J., **19**, 91. Z. physik. Chem., **22**, 237.

In this way a complete precipitation takes place almost at once. Nevertheless, the beakers were allowed to stand on a warm sand bath for half an hour. The precipitate was collected in a Gooch crucible on a layer of purified asbestos.

Standard Alkali.—In order to be able to use the sodium hydroxide both for titration purposes and for preparing the sodium salt solutions of the acids, it was necessary to have an aqueous solution of the alkali, as free as possible from carbonates and other impurities. To prepare such a solution the method of H. W. Cowles, Jr.,¹ is an excellent one.

One hundred grams of sodium hydroxide, purified from alcohol, was dissolved in 100 grams of conductivity water (obtained as above described) and the concentrated solution was allowed to stand in a closed vessel for about a week. By that time practically all the carbonate, etc., was precipitated and there was left a perfectly clear supernatant solution of sodium hydroxide, portions of which were pipetted out and diluted to the proper strength with conductivity water. The dilute solution was then standardized by means of the standard sulphuric acid, and otherwise. When thus prepared, the solution is perfectly free from carbonate, as is shown by the fact that it does not give a precipitate of barium carbonate with barium hydroxide, and that when titrated with indicators, both those that are sensitive and those that are not sensitive to carbonates, the results are practically the same.

Organic Acids.—Kahlbaum's so-called pure acids were almost exclusively employed, and before using them they were all still further purified by one method or another, according to the nature of the acid. Their purity was tested by means of their melting or boiling points, and by titration. No acids were used whose purity could not thus be established.

Sodium Salts of Organic Acids.—These salts, for the most part, were prepared by titrating a solution of the acid (usually about N/128) with a standard solution of sodium hydroxide exactly to neutrality, using a drop of phenolphthalein as indicator. Alizarin is also a good indicator and was used in later work because it is less sensitive to carbonic acid.

¹ J. Am. Chem. Soc., **30**, 1192 (1908).

In a few cases the purified sodium salts were weighed out and made up to the proper strength.

The potassium chloride used for obtaining cell constants was Kahlbaum's purest. To insure its purity it was precipitated from a saturated solution by hydrochloric acid, and then recrystallized three times from conductivity water. Finally, after drying in an oven for some time, it was heated at a moderate temperature for ten or fifteen minutes in a porcelain dish over a Bunsen flame.

Procedure

The molecular conductivities and temperature coefficients were calculated in the usual manner.

For percentage temperature coefficients Schaller's¹ equation,

$$\beta = \frac{\mu_{t_1} - \mu_t}{\mu_{t_1} - (t_1 - t)}$$

was employed.

The equations given above for dissociation and for dissociation constants

$$\alpha = \frac{\mu_v}{\mu_\infty} \text{ and } K = \frac{\alpha^2}{(1 - \alpha)V}$$

were employed in calculating these values for weak monobasic acids. Constants for the strong acids were calculated by a method which will be described later.

Cell Constants.—The usual method, already described by White and Jones,² was followed, a 0.02 N solution of potassium chloride being used for the cells in which the electrodes were fairly wide apart, and a 0.002 N solution for those with the platinum plates close together. The value $\mu_{50} = 129.7$ for the conductivity of the 0.02 N solution at 25° was taken from Kohlrausch, and the value $\mu_{500} = 137.9$ for the 0.002 N solution was found by direct measurement.

The cells were standardized about once a month, but very little change in the constants was found to take place, even in the course of the whole year. Great care was always taken not to change the position of the electrodes, which would of course alter the values of the constants. The following table

¹ Z. physik. Chem., **2**, 561 (1888).

² Am. Chem. J., **42**, 527 (1909).

is typical of the manner in which the results were tabulated, W being the resistance in the rheostat, b the distance on the wire from the point of contact to one end of the wire, and K the cell constants.

Table I.—Cell Constants

Cell	Solution	W	b	K	Mean
VIII	0.02 N	100	559.0	328.82	328.82
		140	475.2	328.84	
		150	458.0	328.80	
VII	0.02 N	80	471.3	184.99	184.97
		84	459.1	184.94	
		88	447.6	184.97	
VI	0.02 N	60	458.0	131.52	131.52
		63	445.9	131.52	
		66	434.5	131.54	
V	0.02 N	40	454.3	86.38	86.38
		42	442.2	88.37	
		44	430.8	86.40	
IV	0.02 N	30	481.6	72.30	72.30
		32	465.5	72.30	
		34	450.4	72.24	
III	0.002 N	200	445.0	44.10	44.10
		210	433.0	44.10	
		220	421.6	44.10	
II	0.002 N	100	443.7	21.94	21.94
		110	420.5	21.95	
		120	469.9	21.94	
I	0.002 N	40	505.6	11.240	11.243
		46	470.5	11.241	
		48	460.0	11.245	
A	0.0005 N	40	451.0	2.381	2.381
		42	439.0	2.381	
		44	427.5	2.381	
V	0.002 N	250	555.7	138.68	
		260	546.0	138.67	
		270	536.5	138.75	
IV	0.002 N	250	511.2	138.66	138.66
		260	501.5	138.60	
		270	492.0	138.64	
II	0.0005 N	340	473.4	143.49	
		350	466.0	143.64	
		370	452.3	143.46	
I	0.0005 N	160	495.0	143.39	143.44
		170	479.9	143.41	
		180	465.6	143.39	

Three readings were taken for each cell, and these agree to within two or three hundredths of a per cent. All the later work, in which the Kohlrausch slide-wire bridge was used, was equally as accurate. In one case cell constants were taken two days in succession, using entirely new solutions on the second day, and here again the agreement was practically perfect.

μ_{∞} for the Sodium Salts of Organic Acids

Whenever it was possible, the μ_{∞} values were obtained by direct measurement, as was done by White and Jones. Such values are given in the following table:

Table II.— μ_{∞} for Sodium Salts

<i>Sodium Trichloracetate</i>				
V	0°	15°	25°	35°
1024	41.96	64.75	82.45	101.98
	$K_t = 41.96 + 1.38t + 0.00952t^2$			
<i>Sodium Cyanacetate</i>				
V	0°	15°	25°	35°
2048	44.65	65.43	86.80	106.0
	$K_t = 44.65 + 1.52t + 0.00668t^2$			
<i>Sodium α-Brompropionate</i>				
V	0°	15°	25°	35°
1024	42.10	65.04	84.26	105.4
2048	44.94*	69.83	89.61*	108.2*
4096	46.63	70.38	90.40	111.2
	$K_t = 44.94 + 1.74t + 0.002t^2$			
<i>Sodium α,β-Dibrompropionate</i>				
V	0°	15°	25°	35°
2048	41.56	64.89	83.24	103.08
	$K_t = 41.56 + 1.44t + 0.009t^2$			
<i>Sodium β-Iodpropionate</i>				
V	0°	15°	25°	35°
2048	41.54	63.70	81.16	102.8
	$K_t = 41.54 + 1.18t + 0.0168t^2$			
<i>Sodium Levulinate</i>				
V	0°	15°	25°	35°
2048	38.47	59.11	75.13	92.94
	$K_t = 38.47 + 1.242t + 0.00898t^2$			

Sodium α-Bromobutyrate

V	0°	15°	25°	35°
1024	41.50	64.16	81.90	101.0
2048	42.46*	65.07	82.53*	102.6*
4096	43.34	66.33	84.32	103.4
	$K_t = 42.46 + 1.32t + 0.0115t^2$			

Sodium Hydroxyisobutyrate

V	0°	15°	25°	35°
2048	40.44	62.36	79.42	97.74
	$K_t = 40.44 + 1.36t + 0.00779t^2$			

Sodium Isovalerate

V	0°	15°	25°	35°
2048	32.31	50.15	63.87	79.33
	$K_t = 32.31 + 1.06t + 0.0081t^2$			

Sodium Caprylate

V	0°	15°	25°	35°
2048	42.67	61.85	77.61	95.77
	$K_t = 42.67 + 1.099t + 0.0120t^2$			

Sodium Benzilate

V	0°	12°	25°	35°
1024	35.1	50.5	69.5	86.2
2048	36.3	52.2	71.5	88.9
4096	35.8	51.7	70.8	88.1
	$K_t = 36.3 + 1.17t + 0.0095t^2$			

Sodium Chlorbenzoate

V	0°	15°	25°	35°
2048	38.03	58.97	75.47	93.18
	$K_t = 38.03 + 1.30t + 0.0078t^2$			

Sodium p-Nitrobenzoate.

V	0°	12°	25°	35°
1024	38.85	55.48	75.71	93.30
2048	39.78	56.28	76.48	95.80
4096	38.91	55.01	75.86	94.00
	$K_t = 39.78 + 1.14t + 0.0133t^2$			

Sodium 1,2,4-Dinitrobenzoate

V	0°	15°	25°	35°
2048	37.80	58.25	74.77	$\left\{ \begin{array}{l} 92.90 \text{ (by titration)} \\ 92.83 \text{ (from dry salt)} \end{array} \right.$
	$K_t = 37.80 + 1.24t + 0.0095t^2$			

Sodium 1,3,5-Dinitrobenzoate

V	0°	15°	25°	35°
2048	37.83	58.30	74.60	92.93 (by titration)
$K_t = 37.83 + 1.24t + 0.0095t^2$				

Sodium 1,3,5-Dinitrobenzoate

V	0°	15°	25°	35°
1024	36.74	56.53	71.81	87.70
2048	37.46	57.56	73.13	89.64
4096	37.98	58.10	74.60	91.70
} (solution of dry salt)				

Sodium 1,2,4-Dihydroxybenzoate

V	0°	15°	25°	35°
2048	39.64	60.72	77.49	95.11
$K_t = 39.64 + 1.337t + 0.00708t^2$				

Sodium 1,2,5-Dihydroxybenzoate

V	0°	15°	25°	35°
2048	39.36	60.58	77.52	95.62
$K_t = 39.36 + 1.324t + 0.0081t^2$				

Sodium p-Sulphamidobenzoate

V	0°	15°	25°	35°
2048	39.30	60.23	76.57	94.00
$K_t = 39.30 + 1.31t + 0.0072t^2$				

In nearly every one of the above cases a concentration of N/2048 alone was used, since it was found by White and Jones that the μ_∞ values of the sodium salts generally occur at this concentration.

The fact that the conductivity of a salt made up by titration and that of the same salt made up from the dry solid agree shows that the titration method is reliable.

It is seen, as would be expected from previous work, that the μ_∞ values of the sodium salts of isomeric acids are practically identical, as, for example, sodium 1,2,4- and 1,3,5-dinitrobenzoates, and sodium 1,2,4- and 1,2,5-dihydroxybenzoates.

Further, the μ_∞ values of the strong acids calculated from the sodium salts are identical with the maximum values of the acids themselves. Trichloroacetic and 1,2,4-dinitrobenzoic acids are examples illustrating this point.

Moreover, we see from the tables that those salts with the largest number of atoms in the anion have the highest μ_{∞} values. The curves expressing the μ_{∞} values for these acids bring this point out still more strikingly.

μ_{∞} *Values of the Acids*

The method by which these values are calculated has already been referred to. Essentially, it is merely a subtracting of the migration velocity value of the sodium ion from the μ_{∞} value of the sodium salt, and an addition of the migration velocity value of the hydrogen ion. In actual practice, the following equation was used:

$$\mu_{\infty}(\text{acid}) = \mu_{\infty}(\text{HCl}) + \mu_{\infty}(\text{Na salt of acid}) - \mu_{\infty}(\text{NaCl})$$

As the values of conductivity between 0° and 25° were, throughout the present work, obtained almost exclusively at 15° , the equations given by White and Jones for calculating the μ_{∞} values of sodium chloride and of hydrochloric acid were made use of in order to obtain the μ_{∞} values of the acids worked with at this temperature.

For sodium chloride at 15° ,

$$\mu_{\infty} = (63.04 + 2.04t + 0.00823t^2) = 95.49$$

and for hydrochloric acid at 15° ,

$$\mu_{\infty} = (245.4 + 6.06t - 0.00776t^2) = 334.5$$

In the table given below are presented the μ_{∞} values of all the acids with which we worked (except dichlorophthalic, tetrachlorophthalic, and meconic acids).

The values for the acids marked with an asterisk were not obtained by means of the method stated above, since they are dibasic and their sodium salts do not yield a maximum value of conductivity at any dilution up to N/4096, which is the highest dilution with which we worked.

A curve, in which the ordinates represent μ_{∞} values and abscissas the number of atoms, was plotted for a large number of monobasic acids, and by placing the dibasic acids in their

proper position on this curve (according to the number of atoms present) their μ_{∞} values can be obtained (see Fig. I).

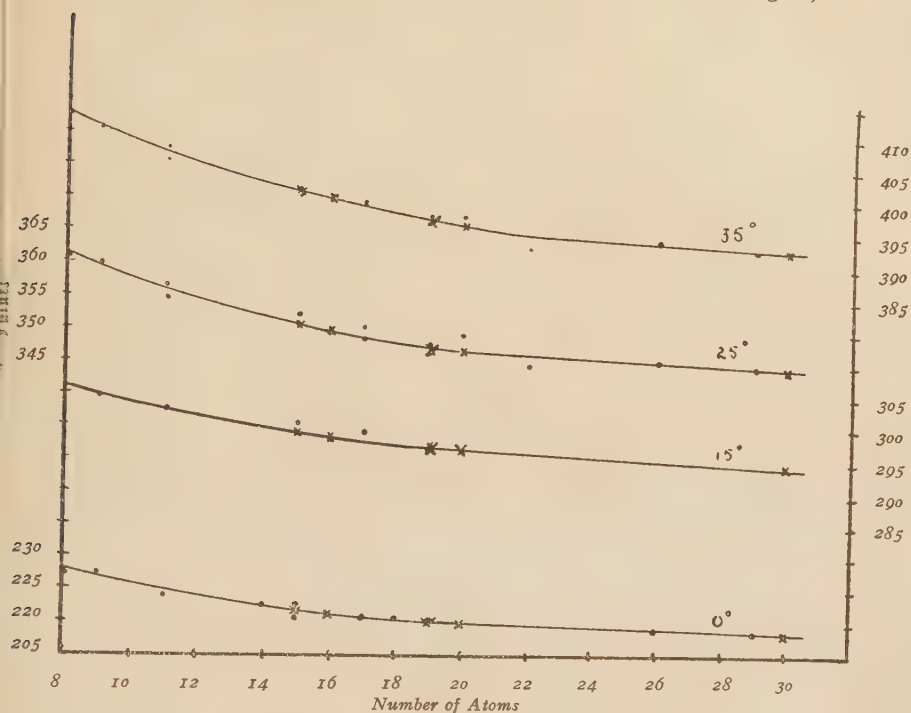


Fig. I.—Limiting Conductivities

Table III.— μ_{∞} Values of the Acids

Acid	$\mu_{\infty} 0^{\circ}$	$\mu_{\infty} 12^{\circ}$	$\mu_{\infty} 15^{\circ}$	$\mu_{\infty} 25^{\circ}$	$\mu_{\infty} 35^{\circ}$
Trichloroacetic.....	224.8	...	303.9	355.9	406.4
Cyanoacetic.....	271.1	...	304.5	360.0	410.0
Benzilic.....	218.7	280.5	...	344.7	392.9
α -Bromopropionic.....	229.0	...	308.9	363.6	415.2
α,β -Dibromopropionic.....	223.9	...	303.9	356.4	407.0
β -Iodopropionic.....	223.9	...	302.8	354.4	406.8
Levulinic.....	220.9	...	298.2	348.3	396.9
α -Brombutyric.....	230.7	...	304.1	357.5	407.4
Hydroxyisobutyric.....	222.8	...	301.4	352.6	401.7
Isovaleric.....	214.7	...	289.2	337.1	383.3
Caprylic.....	225.1	...	300.9	350.8	399.8
<i>l</i> -Tartaric*.....	221.0	...	298.8	350.0	399.9
Thiodiglycolic*.....	221.6	...	300.2	351.1	401.0

Table III.—(Continued)

Acid	μ_{∞} 0°	μ_{∞} 12°	μ_{∞} 15°	μ_{∞} 25°	μ_{∞} 35°
Tricarballic*	219.9	...	296.7	347.6	396.8
<i>p</i> -Nitrobenzoic	222.2	284.6	...	349.7	399.8
1,2,4-Dinitrobenzoic	200.0	...	297.3	347.9	396.8
1,3,5-Dinitrobenzoic	220.2	...	297.4	347.4	396.9
<i>o</i> -Chlorbenzoic	220.4	...	301.8	348.7	397.2
1,2,4-Dihydroxybenzoic	222.0	...	299.8	350.7	399.1
1,2,5-Dihydroxybenzoic	221.8	...	299.6	350.7	399.6
<i>p</i> -Sulphamidobenzoic	221.7	...	299.3	349.8	398.0
Benzenesulphonic	228.0	...	309.0	359.0	410.3
<i>p</i> -Toluenesulphonic	210.6	269.7	...	332.7	379.3
<i>m</i> -Nitrobenzenesulphonic	204.5	...	^{16°} 275.5	223.5	369.4
1,2,4-Nitrotoluenesulphonic	200.5	...	276.5	318.4	361.9
Camphoric*	218.3	279.8	...	344.5	392.5
Uric*	221.0	...	298.8	350.0	399.9
Cyanuric	...	...	...	...	405.0

RESULTS

Trichloroacetic Acid, CCl_3COOH

The acid is very hygroscopic, so it was not dried thoroughly after recrystallization from water, but was made up to approximate strength and then standardized by titration.

Ostwald¹ determined the conductivity of the acid at 25° and comparison of his results with our own at the same temperature shows a fairly close agreement, especially at the higher dilutions:

Ostwald		From Tables IV and VI
<i>V</i>	μ_v 25°	μ_v 25°
32	323.0	322.46
128	341.0	344.90
512	353.7	353.96
1024	356.0	355.94

The relation of trichloroacetic acid to acetic acid, monochloroacetic acid, and other acetic acid derivatives, was brought out with sufficient clearness by Ostwald, and need not be discussed here. The acid itself, however, is of especial interest, because it is a very strong electrolyte (very nearly as strong as hydrochloric acid).

We see from Table VI that the acid is entirely dissociated at N/2048. The μ_{∞} value ($\mu_{\infty} = 358$) given by Ostwald.

¹ Z. physik. Chem., **3**, 177 (1889).

is greater than any of the conductivity values given by him, and, therefore, his percentage dissociation values do not reach a maximum; but we find that μ_{∞} , as obtained from the sodium salt, agrees very closely with the maximum value for conductivity of the acid at 25° (at N/2048).

Table IV.—Molecular Conductivity

V	0°	15°	25°	35°
8	193.02	256.24	298.40	334.67
32	208.75	277.67	322.46	363.69
128	221.73	297.62	344.90	389.83
512	223.65	302.33	353.96	403.45
1024	224.77	303.94	355.94	406.44
2048	221.52	300.21	349.57	397.46

Table V.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.25	2.20	4.22	1.65	3.63	1.22
32	4.60	2.20	4.48	1.61	4.12	1.28
128	5.06	2.28	4.73	1.59	4.49	1.30
512	5.25	2.35	5.16	1.70	4.95	1.40
1024	5.28	2.35	5.20	1.71	5.05	1.42
2048	5.24	2.37	4.94	1.65	4.79	1.37

μ_{∞} Values (measured directly)

V	0°	15°	25°	35°
1024	224.77	303.94	355.94	406.44

μ_{∞} Values (from sodium salt)

V	0°	15°	25°	35°
1024	223.67	303.86	355.65	405.91

Table VI.—Percentage Dissociation

V	0°	15°	25°	35°
8	85.87	84.31	83.83	82.34
32	92.87	91.36	90.59	89.88
128	98.65	97.92	96.90	95.91
312	99.50	99.47	99.44	99.26
1024	100.00	100.00	100.00	100.00

Cyanacetic Acid, $\text{CH}_2(\text{CN})\text{COOH}$

The acid was easily purified by recrystallization from water, and was dried over sulphuric acid in a vacuum desiccator. The pure, dry acid has a melting point of 65°.

It is of interest to note the effect of the cyanogen group when introduced into acetic acid, and also to compare its effect with that of other groups.

<i>V</i>	<i>Acetic Acid</i> White and Jones ¹		<i>Monochloroacetic Acid</i> Ostwald ²		<i>Monobromoacetic Acid</i> Ostwald ²	
	$\mu\eta$ 25°	α 25°	$\mu\eta$ 25°	α 25°	$\mu\eta$ 25°	α 25°
8	4.342	1.20	...	...	...	...
32	8.699	2.41	72.4	19.94	68.7	18.95
128	17.11	4.74	127.7	35.2	122.3	33.7
512	33.24	9.21	205.8	56.8	199.2	55.0
1024	45.87	12.71	249.2	68.7	241.2	66.6
2048	63.00	17.45	...	...	...	...
	$K^3 = 0.184$		$K = 15.5$		$K = 13.8$	

<i>V</i>	<i>Phenylacetic Acid</i> White and Jones ⁴		<i>Cyanacetic Acid</i> From Tables VII and IX	
	$\mu\eta$ 25°	α 25°	$\mu\eta$ 25°	α 25°
8	...	...	59.53	16.54
32	14.15	4.05	106.47	29.58
128	27.96	8.01	178.86	49.68
512	52.39	14.97	259.64	72.12
1024	71.63	20.52	291.56	80.99
2048	95.50	27.36	314.3	87.30
	$K = 0.545$		$K = 36.3$	

The strong negative character and influence of the cyanogen group is strongly brought out by the fact that the constant for cyanacetic acid is but little less than that for monobromoacetic acid, and that it is very nearly two hundred times as great as that for acetic acid.

Table VII.—Molecular Conductivity

<i>V</i>	0°	15°	25°	35°
8	38.27	51.66	59.53	66.15
32	68.70	92.26	106.47	118.79
128	114.23	154.10	178.86	199.67
512	164.90	223.37	259.64	293.00
1024	187.49	252.59	291.56	332.00
2048	199.90	270.40	314.30	356.60

¹ Am. Chem. J., **44**, 165 (1910).

² Z. physik. Chem., **3**, 178 (1889).

³ NOTE.— K , throughout this work, means constant $\times 10^4$.

⁴ Am. Chem. J., **44**, 168 (1910).

Table VIII.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.893	2.33	0.787	1.52	0.662	1.11
32	1.67	2.29	1.42	1.54	1.23	1.16
128	2.66	2.33	2.48	1.61	2.08	1.16
512	3.90	2.36	3.63	1.62	3.04	1.17
1024	4.35	2.32	3.97	1.57	4.04	1.39
2048	4.70	2.35	4.39	1.62	4.23	1.35

Table IX.—Percentage Dissociation

V	0°	15°	25°	35°
8	16.86	16.97	16.54	16.13
32	30.26	30.30	29.58	28.97
128	50.31	50.60	49.68	48.70
512	72.63	73.36	72.12	71.46
1024	82.58	82.96	80.99	80.98
2048	88.04	88.80	87.30	86.97

Table X.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	43	42	41	39
32	41	40	39	37
128	40	39	38	36
512	38	37	36	35
1024	38	36	35	34
2048	32	31	29	28

Benzilic or Diphenylglycolic Acid, (C₆H₅)₂C(OH)COOH

The ordinary method of recrystallization was used for purifying this acid (melting point, 150°).

Here we have the effect of both hydroxyl and phenyl groups, and the result is an acid ($K_{25^\circ} = 9.20$) which is fifty times as strong as acetic acid ($K_{25^\circ} = 0.184$)¹ and six times as strong as glycolic acid ($K_{25^\circ} = 1.52$).²

Table XI.—Molecular Conductivity

V	0°	12°	25°	35°
128	63.8	81.7	101.5	115.0
512	106.4	138.3	169.5	186.9
1024	133.6	169.8	208.4	237.1
2048	152.3	193.0	233.7	260.6

¹ Am. Chem. J., 44, 168 (1910).² Ostwald: Z. physik. Chem., 3, 183 (1889).

Table XII.—Temperature Coefficients

V	0°–12°		12°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.52	2.38	1.50	1.84	1.35	0.93
512	2.66	2.50	2.24	1.62	1.94	1.04
1024	3.02	2.26	2.97	1.75	2.87	1.23
2048	3.39	2.23	3.13	1.62	2.69	1.03

Table XIII.—Percentage Dissociation

V	0°	12°	25°	35°
128	29.17	29.08	29.45	29.27
512	48.64	49.24	48.60	47.57
1024	61.08	60.44	60.46	60.20
2048	69.63	68.71	67.81	64.82

Table XIV.—Dissociation Constants $\times 10^4$

V	0°	12°	25°	35°
128	9.38	9.10	9.60	9.46
512	9.00	9.32	8.97	8.43
1024	9.36	9.02	9.02	8.89
2048	7.80	7.37	6.97	5.83

 α -Brompropionic Acid, $\text{CH}_3\text{CHBr.COOH}$

The acid was purified by distillation and was then a clear colorless liquid, boiling at 205°. The calculated quantity for making up a N/32 solution was accurately weighed out into a weighing bottle and then poured into a flask and diluted. A portion of this dilute solution, enough to make a N/1024 solution, was titrated in order to form the sodium salt, and also to be sure of its normality.

Table XV.—Molecular Conductivity

V	0°	15°	25°	35°
32	38.00	49.38	58.86	61.5
128	77.10	100.00	114.4	125.9
512	124.7	164.1	186.8	206.7
1024	151.7	200.8	229.5	257.0
2048	171.5	227.4	262.0	295.3

Table XVI.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.76	2.00	0.65	1.31	0.56	1.00
128	1.53	1.99	1.44	1.44	1.05	0.92
512	2.63	2.11	2.27	1.38	1.99	1.07
1024	3.27	2.16	2.87	1.43	2.75	1.17
2048	3.70	2.16	3.46	1.52	3.33	1.27

Table XVII.—Percentage Dissociation

V	0°	15°	25°	35°
32	16.60	15.99	15.38	14.81
128	33.67	32.37	31.47	30.33
512	54.45	53.13	50.21	49.79
1024	66.25	65.01	62.98	61.90
2048	77.52	73.62	72.06	71.12

Table XVIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
32	10.3	10.2	8.7	8.0
128	13.4	13.2	11.3	10.3
512	12.7	13.1	9.9	9.6
1024	12.7	13.5	10.6	9.8
2048	13.1	11.9	11.4	8.4

 β -Iodpropionic Acid, $\text{CH}_2\text{ICH}_2\text{COOH}$

Several recrystallizations were necessary in order to purify this acid, as it decomposes on standing in the presence of light, and the acid as it came from Kahlbaum was found to be quite impure. Its melting point when pure is 85°.

There is also quite a rapid decomposition of the acid when its solution is placed in the cells in the presence of the platinum electrodes, especially at 35°. This made it necessary to refill the cells with fresh solution after the measurements were taken at each temperature.

The decomposition just spoken of may be an explanation of the increase in its temperature coefficients between 25° and 35°, as compared with those from 15°-25°.

Table XIX.—Molecular Conductivity

V	0°	15°	25°	35°
8	6.30	8.42	9.73	11.12
32	12.57	16.81	19.37	21.98
128	23.79	31.86	36.67	41.69
512	44.36	59.47	68.42	78.04
1024	58.61	78.67	91.05	104.24
2048	76.55	102.87	118.35	135.40

Table XX.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.141	2.23	0.131	1.56	0.139	1.43
32	0.283	2.25	0.256	1.52	0.261	1.35
128	0.538	2.26	0.482	1.51	0.502	1.37
512	1.007	2.27	0.895	1.51	0.964	1.41
1024	1.337	2.28	1.238	1.57	1.319	1.45
2048	1.755	2.29	1.548	1.51	1.705	1.44

Table XXI.—Percentage Dissociation

V	0°	15°	25°	35°
8	2.836	2.781	2.752	2.744
32	5.657	5.552	5.478	5.425
128	10.71	10.56	10.37	10.29
512	19.97	19.64	19.35	19.26
1024	26.38	25.98	25.75	25.73
2048	34.46	33.98	33.47	33.42

Table XXII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	1.04	1.00	0.97	0.97
32	1.04	1.02	0.99	0.97
128	1.00	0.97	0.94	0.93
512	0.97	0.94	0.91	0.90
1024	0.92	0.89	0.87	0.87
2048	0.89	0.85	0.82	0.82

Levulinic or β -Acetylpropionic Acid, $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COOH}$

The melting point of the acid is $32^\circ.5$ – 33° , so that it was purified by solidifying it, and pressing on a porous plate.

The relation of levulinic acid to those just preceding is brought out by the following tables:

<i>Propionic Acid</i> White and Jones ¹			<i>α-Bromopropionic Acid</i> From Tables XV and XVII		
V	μ_v 25°	α 25°	μ_v 25°	α 25°	
8	3.70	1.05	...	...	
32	7.44	2.10	58.86	15.38	
128	14.57	4.12	114.40	31.47	
512	28.40	8.02	186.40	50.21	
1024	38.94	11.00	229.50	62.98	
2048	53.47	15.10	262.00	72.06	
	$K = 0.138$			$K = 10.4$	

<i>β-Iodopropionic Acid</i> From Tables XIX and XXI			<i>Levulinic Acid</i> From Tables XXIII and XXV		
V	μ_v 25°	α 25°	μ_v 25°	α 25°	
8	9.73	2.752	4.857	1.39	
32	19.37	5.478	9.71	2.79	
128	36.67	10.37	19.08	5.48	
512	68.42	19.35	36.37	10.44	
1024	91.05	25.75	49.85	14.31	
2048	118.35	33.47	66.24	19.02	
	$K = 0.977$			$K = 0.243$	

As we would expect, propionic acid has the lowest values for conductivity, for dissociation and for the constant; and levulinic acid, with an acetyl group in place of one of the hydrogens of propionic acid, has the next higher values. The bromine substitution product is seen to be one hundred times as strong as that containing iodine, which, in turn, is over four times as strong as the acetyl derivative.

Table XXIII.—Molecular Conductivity

V	0°	15°	25°	35°
8	2.939	4.114	4.851	5.539
32	5.85	8.24	9.71	11.10
128	11.57	16.13	19.08	21.84
512	22.06	30.78	36.37	41.68
1024	29.81	41.92	49.85	56.99
2048	39.41	56.31	66.24	76.53

¹ Am. Chem. J., 44, 165 (1910).

Table XXIV.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.0783	2.66	0.0737	1.79	0.0688	1.42
32	0.160	2.74	0.147	1.78	0.139	1.43
128	0.304	2.63	0.295	1.83	0.276	1.45
512	0.581	2.63	0.559	1.82	0.531	1.46
1024	0.807	2.71	0.793	1.89	0.714	1.43
2048	1.126	2.86	0.993	1.76	1.029	1.55

Table XXV.—Percentage Dissociation

V	0°	15°	25°	35°
8	1.33	1.38	1.39	1.40
32	2.65	2.76	2.79	2.80
128	5.24	5.41	5.48	5.50
512	9.99	10.32	10.44	10.50
1024	13.50	14.06	14.31	14.36
2048	17.84	18.89	19.02	19.28

Table XXVI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	0.224	0.234	0.245	0.249
32	0.225	0.238	0.250	0.252
128	0.226	0.235	0.248	0.250
512	0.217	0.226	0.238	0.241
1024	0.206	0.219	0.233	0.235
2048	0.189	0.209	0.218	0.225

 α -Brombutyric Acid, $\text{CH}_3\text{CH}_2\text{CHBrCOOH}$

This acid is very similar in almost every respect to α -brompropionic acid; it is a liquid, boiling at 215° , which was purified by distillation, and was weighed out and made up to proper normality in the usual way. When we compare its conductivity and dissociation with α -brompropionic acid we see that the conductivity, dissociation, and constant of the latter, though somewhat smaller, are yet not very different.

Table XXVII.—Molecular Conductivity

V	0°	15°	25°	35°
32	42.75	54.70	61.0	66.42
128	84.94	109.5	122.8	134.3
512	133.7	173.2	195.2	214.9
1024	160.6	209.3	239.8	266.0
2048	180.7	238.0	275.0	305.9

Table XXVIII.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	0.793	1.86	0.630	1.15	0.542	0.889
128	1.64	1.93	1.33	1.21	1.15	0.937
512	2.63	1.97	2.20	1.27	1.97	1.01
1024	3.25	2.02	3.05	1.46	2.62	1.09
2048	3.82	2.11	3.70	1.55	3.09	1.12

Table XXIX.—Percentage Dissociation

V	0°	15°	25°	35°
32	18.53	17.99	17.06	16.30
128	36.82	36.00	34.35	32.97
512	57.97	56.92	54.59	52.74
1024	69.61	68.82	67.08	65.30
2048	78.32	78.26	76.91	75.09

Table XXX.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
32	13.1	13.2	11.0	10.1
128	16.8	17.2	14.0	12.7
512	15.6	16.4	12.8	11.5
1024	15.6	17.0	13.2	12.0
2048	13.8	16.6	12.5	11.1

Hydroxyisobutyric Acid, $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$

Hydroxyisobutyric acid sublimes at 50° and the fresh sublimate melts at 79° .

Ostwald obtained the conductivity of this acid at 25° , and for the sake of comparison his values are given below:

V	Ostwald ¹		From Tables XXXI and XXXIII	
	μ_{25°	α_{25°	μ_{25°	α_{25°
32	20.05	5.65	20.19	5.75
128	38.86	10.95	39.18	11.15
512	73.49	20.70	73.16	20.82
1024	99.52	28.05	97.00	27.61
	$K = 1.06$		$K = 1.06$	

The conductivities agree to within five-tenths of a per cent., except at N/2048. The dissociation given by Ostwald is less

¹ Z. physik. Chem., **3**, 197 (1889).

(except at N/2048), since he used the value $\mu_{\infty} = 355$, whereas our own value of μ_{∞} is 352.6. The mean value for the constant in both cases, however, is the same.

As to the relation of hydroxyisobutyric acid to butyric acid, its constant ($K = 1.06$) is a little less than seven times as great as that of butyric acid ($K = 0.163$). α -Bromobutyric acid has a constant ($K = 12.7$), about twelve times as large as the hydroxyl derivative.

Table XXXI.—Molecular Conductivity

<i>V</i>	0°	15°	25°	35°
8	6.075	8.553	10.147	11.576
32	12.11	17.04	20.19	22.97
128	23.50	33.04	39.18	44.65
512	44.06	61.74	73.16	83.41
1024	58.80	81.95	97.00	111.60
2048	76.78	106.95	126.20	144.07

Table XXXII.—Temperature Coefficients

<i>V</i>	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.165	2.72	0.159	1.86	0.143	1.41
32	0.329	2.71	0.315	1.85	0.278	1.38
128	0.636	2.71	0.614	1.86	0.547	1.40
512	1.18	2.68	1.14	1.85	1.03	1.40
1024	1.54	2.62	1.51	1.84	1.46	1.50
2048	2.01	2.62	1.93	1.80	1.79	1.41

Table XXXIII.—Percentage Dissociation

<i>V</i>	0°	15°	25°	35°
8	2.75	2.838	2.89	2.89
32	5.47	5.653	5.75	5.74
128	10.62	10.96	11.15	11.15
512	19.92	20.48	20.82	20.84
1024	25.58	27.19	27.61	27.88
2048	34.70	35.48	35.92	36.00

Table XXXIV.—Dissociation Constants $\times 10^4$

<i>V</i>	0°	15°	25°	35°
8	0.97	1.05	1.08	1.08
32	0.99	1.06	1.10	1.10
128	0.99	1.17	1.09	1.09
512	0.97	1.03	1.07	1.07
1024	0.94	0.99	1.03	1.08
2048	0.90	0.95	0.98	0.99

Isovaleric Acid, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{COOH}$

This acid, boiling at 176° , was fractionally distilled and diluted in the usual manner for nonvolatile liquids. Its relation to the other acids of the aliphatic series is discussed under caprylic acid.

Table XXXV.—Molecular Conductivity

V	0°	15°	25°	35°
8	2.474	3.229	3.666	4.044
32	5.052	6.591	7.493	6.262
128	9.832	12.92	14.69	16.19
512	19.023	24.81	28.13	31.03
1024	26.264	34.22	38.49	42.98
2048	34.804	45.28	51.69	58.02

Table XXXVI.—Temperature Coefficients

V	$0^\circ-15^\circ$		$15^\circ-25^\circ$		$25^\circ-35^\circ$	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.0503	2.03	0.0473	1.35	0.0378	1.03
32	0.1026	2.04	0.0902	1.36	0.0769	1.03
128	0.2044	2.07	0.1767	1.37	0.1506	1.03
512	0.3856	2.03	0.3318	1.34	0.291	1.03
1024	0.530	2.02	0.427	1.25	0.449	1.16
2048	0.699	2.06	0.640	1.41	0.634	1.22

Table XXXVII.—Percentage Dissociation

V	0°	15°	25°	35°
8	1.15	1.117	1.09	1.06
32	2.35	2.279	2.22	2.16
128	4.59	4.467	4.36	4.22
512	8.86	8.579	8.34	8.10
1024	12.23	11.83	11.42	11.22
2048	16.21	15.66	15.33	15.14

Table XXXVIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	0.167	0.154	0.150	0.142
32	0.177	0.162	0.158	0.149
128	0.172	0.159	0.155	0.145
512	0.168	0.154	0.148	0.139
1024	0.166	0.151	0.144	0.138
2048	0.153	0.138	0.136	0.132

Caprylic Acid, $\text{CH}_3(\text{CH}_2)_6\text{COOH}$

The easiest method of purifying this acid, which melts at 16.5° , was found to be to solidify it and press out the solid on a porous plate. Being a nonvolatile liquid at ordinary temperatures, solutions of it were made up in a manner similar to that employed for α -brompropionic and α -brombutyric acids.

Table XXXIX.—Molecular Conductivity

V	0°	15°	25°	35°
512	...	...	27.79	31.07
1024	24.39	32.76	37.84	42.35
2048	32.84	44.08	51.08	56.89

Table XL.—Temperature Coefficients

V	$0^\circ-15^\circ$		$15^\circ-25^\circ$		$25^\circ-35^\circ$	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	...	..	...	..	0.328	1.18
1024	0.558	2.29	0.508	1.55	0.453	1.17
2048	0.749	2.28	0.700	1.58	0.571	1.12

Table XLI.—Percentage Dissociation

V	0°	15°	25°	35°
512	...	...	7.96	7.80
1024	10.84	10.89	10.84	10.64
2048	14.60	14.65	14.63	14.29

Table XLII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	...	...	0.134	0.129
1024	0.129	0.130	0.129	0.124
2048	0.122	0.123	0.123	0.116

We would expect, since caprylic acid is one of the higher aliphatic acids, that its conductivity and dissociation would be less than that of those aliphatic acids with less complex molecules, and such is the case, as was first shown by Ostwald,¹ and as can be seen by comparison of its values with the values in the following tables:

¹ Z. physik. Chem., **3**, 176 (1889).

V	Acetic Acid White and Jones ¹		Propionic Acid White and Jones		n-Butyric Acid White and Jones	
	μ_D 25°	α 25°	μ_D 25°	α 25°	μ_D 25°	α 25°
512	33.24	9.21	28.40	8.00	29.86	8.44
1024	45.87	12.71	38.94	11.00	41.22	11.64
2048	63.00	17.45	53.47	15.10	59.20	16.15
	$K = 0.175$		$K = 0.133$		$K = 0.163$	
V	Valeric Acid Ostwald ²		Isovaleric Acid From Tables XXXV and XXXVII		Cobutylic Acid From Tables XXXIX and XLI	
	μ_D 25°	α 25°	μ_D 25°	α 25°	μ_D 25°	α 25°
512	15.7	4.44	28.13	8.34	27.79	7.96
1024	30.4	8.59	38.49	11.42	37.84	10.84
2048	41.9	11.83	51.69	15.33	51.08	14.63
	$K = 0.161$		$K = 0.149$		$K = 0.129$	

1-Tartaric Acid, $\text{HOOC}(\text{CHOH})_2\text{COOH}$

This acid was recrystallized several times from water, and finally dried at 105° in a hot-air bath. The N/8 solution of the pure acid was tested as to its optical activity with a polariscope. The amount of rotation indicated that the acid was pure.

The constant of this acid ($K_{25^\circ} = 10.7$) at 25°, as compared with that obtained by White and Jones for racemic acid ($K_{25^\circ} = 10.8$), indicates a close relationship in chemical activity as well as in structure. Ostwald's values of conductivity, dissociation, etc., of both *d*- and *l*-tartaric acids are given below, and it is seen that though his values of conductivity are not very concordant with our own, the values for the constant are not very different.

V	<i>d</i> -Tartaric Acid Ostwald			1-Tartaric Acid Ostwald		
	μ_D 25°	α 25°	K 25°	μ_D 25°	α 25°	K 25°
32	57.60	16.20	9.8	57.6	16.19	9.7
128	106.2	29.85	9.9	105.6	29.7	9.7
512	184.5	51.80	10.9	183.2	51.5	10.7
1024	236.0	66.0	12.7	234.0	65.8	12.3
2048	291.0	81.8	17.9	289.5	81.4	17.4
	$K = 9.7$			$K = 9.7$		

¹ Am. Chem. J., **44**, 165 (1910).

² Z. physik. Chem., **3**, 175 (1889).

We notice that the constants given by Ostwald increase rapidly with dilution. The same is true of our own, and is no doubt due to the fact that the acid is dibasic and the second hydrogen begins to dissociate at about $N/128$. Ostwald's figure for the constant, $K_{25^\circ} = 9.7$, includes only the values at $N/32$ and $N/128$. If all the values except that at $N/2048$ are averaged, then his constant would be $K_{25^\circ} = 10.6$, which agrees closely with our own, $K_{25^\circ} = 10.7$, averaged in a similar manner.

Table XLIII.—Molecular Conductivity

V	0°	15°	25°	35°
8	15.64	22.58	26.93	31.12
32	34.18	49.03	58.72	67.65
128	62.81	90.12	107.4	123.5
512	109.3	156.8	186.9	213.0
1024	136.0	192.0	229.4	261.6
2048	171.7	241.0	285.4	325.5

Table XLIV.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.463	2.96	0.435	1.93	0.419	1.55
32	0.990	2.94	0.969	1.98	0.893	1.52
128	1.89	3.00	1.73	1.92	3.61	1.47
512	3.17	2.90	3.01	1.92	2.61	1.40
1024	3.73	2.75	3.74	1.95	3.22	1.40
2048	4.62	2.69	4.44	1.84	4.09	1.40

μ_∞ Values (from graph)

	0°	15°	25°	35°
	221.0	298.8	350.0	399.9
$K_{15^\circ} = [221.0 + (5.28 \times 15) - (0.00486 \times 225)] = 299.1$				

Table XLV.—Percentage Dissociation

V	0°	15°	25°	35°
8	7.08	7.56	7.69	7.78
32	15.47	16.41	16.78	16.91
128	28.42	30.16	30.68	30.88
512	49.46	52.48	53.40	53.25
1024	61.54	64.26	65.54	65.40
2048	77.69	80.66	81.54	81.38

Table XLVI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
8	6.7	7.7	8.0	8.2
32	8.9	10.1	10.6	10.8
128	8.8	10.2	10.6	10.8
512	9.5	11.3	12.0	11.8
1024	9.6	11.3	12.2	12.1
2048	13.2	16.4	17.6	17.4

Thiodiglycolic Acid, $S(CH_2COOH)_2$

Thiodiglycolic acid ($K_{25}^\circ = 4.8$), as Ostwald¹ showed, is weaker than diglycolic acid ($K_{25}^\circ = 11.0$), the introduction of sulphur in the place of oxygen decreasing the dissociation. Both acids, however, are stronger than either glycolic acid ($K_{25}^\circ = 1.52$) or thioglycolic acid ($K_{25}^\circ = 2.25$), which bear the opposite relation to each other as compared with diglycolic and thiodiglycolic acids.

Ostwald¹ calculated the constants of the latter by a formula somewhat different from that representing the ordinary dilution law:

$$\frac{\alpha^3}{(1 - \alpha)V^2} = K$$

From this equation he obtained the value $K_{25}^\circ = 4.8$ for thiodiglycolic acid, whereas we found the value $K_{25}^\circ = 6.51$ for the same acid, calculated by means of the ordinary dilution law. A glance at Table L will show that the constants thus obtained are fairly good up to N/2048, where evidently the second hydrogen begins to dissociate appreciably.

If the above equation is used we obtain the values:

V	K_{25}°	V	K_{25}°
8	607	512	504
32	257	1024	338
128	113	2048	255

from which it is readily seen that the ordinary law can be better applied to our values.

¹ Z. physik. Chem., **3**, 187 (1889).

Table XLVII.—Molecular Conductivity

<i>v</i>	0°	15°	25°	35°
8	15.70	21.40	25.00	28.16
32	28.86	39.38	46.27	52.18
128	52.79	72.42	84.80	96.00
512	93.31	127.47	148.93	169.03
1024	119.93	164.00	191.30	216.13
2048	152.20	207.38	242.65	275.70

Table XLVIII.—Temperature Coefficients

<i>v</i>	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.38	2.42	0.36	1.68	0.316	1.26
32	0.70	2.43	0.69	1.75	0.591	1.28
128	1.31	2.48	1.24	1.71	1.12	1.32
512	2.28	2.44	2.15	1.68	2.01	1.35
1024	2.94	2.45	2.73	1.67	2.48	1.30
2048	3.68	2.42	3.53	1.70	3.31	1.36

 μ_{∞} Values (from graph)

<i>v</i>	0°	15°	25°	35°
2048	221.6	300.2	350.1	401.0

$K_t = [221.6 + (532 \times 15) - (0.00544 \times 225)] = 300.2$

Table XLIX.—Percentage Dissociation

<i>v</i>	0°	15°	25°	35°
8	7.09	7.13	7.12	7.02
32	13.03	13.11	13.17	13.01
128	23.83	24.12	24.14	23.94
512	42.12	42.45	42.39	42.15
1024	54.14	54.61	54.46	53.90
2048	68.70	69.06	69.10	68.76

Table L.—Dissociation Constants $\times 10^4$

<i>v</i>	0°	15°	25°	35°
8	6.77	6.85	6.82	6.63
32	6.10	6.18	6.24	6.08
128	5.83	5.99	6.00	5.89
512	5.99	6.11	6.09	6.00
1024	6.24	6.33	6.36	6.16
2048	7.36	7.53	7.54	7.39

Tricarballic Acid, $\text{HOOC.CH}(\text{CH}_2\text{COOH})_2$

The acid was recrystallized in the usual manner. It melts at 165°.

Walden¹ and Walker² both obtained the conductivity of this acid at 25°. Their values are given in the following tables:

Walden		Walker	
V	μ_v 25°	V	μ_v 25°
32	28.33	33.4	29.1
128	54.8	133.6	55.6
512	102.7	534.0	103.0
1024	139.0	1068.0	135.8
$K = 2.2$		$K = 2.24$	

The fact that the constants given in Table LIV agree so well seems to indicate that the acid dissociates all the way up to N/2048 as if it were a monobasic acid.

Table LI.—Molecular Conductivity

V	0°	15°	25°	35°
8	8.26	11.73	14.05	16.24
32	16.39	23.41	8.02	32.38
128	31.82	45.13	53.98	62.28
512	59.35	83.65	99.99	115.38
1024	78.79	110.53	131.67	152.40
2048	103.03	143.90	170.85	196.65

Table LII.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	0.231	2.79	0.231	1.97	0.218	1.55
32	0.468	2.86	0.461	1.97	0.436	1.56
128	0.887	2.79	0.885	1.96	0.830	1.54
512	1.63	2.74	1.63	1.95	1.54	1.54
1024	2.12	2.68	2.11	1.91	2.06	1.57
2048	2.73	2.65	2.70	1.87	2.58	1.51

μ_∞ Values (determined graphically)

	0°	15°	25°	35°
	219.9	296.7	347.6	396.8
$K_{15} = [219.9 \times (5.22 \times 15) - (0.00438 \times 225)] = 297.2$				

¹ Z. physik. Chem., **10**, 563 (1892).

² J. Chem. Soc., **61**, 707 (1892).

Table LIII.—Percentage Dissociation

V	0°	15°		25°	35°
		from graph	from equation		
8	3.76	3.95	3.95	4.04	4.09
32	7.45	7.89	7.88	8.07	8.16
128	14.47	15.21	15.18	15.53	15.69
512	26.99	28.19	28.14	28.77	29.06
1024	35.83	37.25	37.18	37.88	38.39
2048	46.85	48.49	48.41	49.15	49.54

Table LIV.—Dissociation Constants $\times 10^4$

V	0°	15°		25°	35°
		from graph	from equation		
8	1.84	2.03	2.03	2.13	2.18
32	1.87	2.11	2.11	2.21	2.27
128	1.91	2.13	2.12	2.23	2.28
512	1.95	2.16	2.15	2.27	2.33
1024	1.95	2.16	2.15	2.25	2.34
2048	2.02	2.25	2.22	2.32	2.38

p-Nitrobenzoic Acid, $\text{O}_2\text{NC}_6\text{H}_4\text{COOH}$

The acid was purified by dissolving in alcohol and precipitating by adding a large quantity of water and stirring rapidly. The melting point was found to be 240°.

The constant for *p*-nitrobenzoic acid ($K_{25^\circ} = 4.14$) is much greater, in fact, nearly seven times greater, than that for benzoic acid ($K_{25^\circ} = 0.686$).

Table LV.—Molecular Conductivity

V	0°	12°	25°	35°
512	79.1	104.0	128.9	148.3
1024	99.9	131.5	163.4	187.4
2048	126.8	165.9	205.4	235.4

Table LVI.—Temperature Coefficients

V	0°–12°		12°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	2.08	2.63	1.92	1.85	1.95	1.51
1024	2.63	2.63	2.46	1.87	2.40	1.47
2048	3.26	2.57	3.04	1.83	3.00	1.46

Table LVII.—Percentage Dissociation

V	0°	12°	25°	35°
512	35.59	36.55	36.86	37.12
1024	44.93	46.20	46.73	46.86
2048	55.47	58.30	58.73	58.87

Table LVIII.—Dissociation Constants $\times 10^4$

V	0°	12°	25°	35°
512	3.84	4.11	4.30	4.28
1024	3.58	3.87	4.00	4.03
2048	3.43	3.98	4.08	4.11

1,2,4-Dinitrobenzoic Acid, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{COOH}$

The acid was purified by the ordinary method of recrystallization and melted at 179° .

The introduction of two nitro groups into the ortho and meta positions of benzoic acid seems to produce a marked effect on its conductivity, and forms an acid which can be classed among the strong electrolytes. Its constants will be spoken of later in connection with those of the other strong acids.

Table LIX.—Molecular Conductivity

V	0°	15°	25°	35°
32	166.51	212.12	238.54	260.00
128	199.23	262.30	299.83	336.35
512	214.97	288.23	334.50	379.00
1024	218.60	293.40	343.55	391.02
2048	220.00	297.30	347.91	396.83

Table LX.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	3.04	1.83	2.64	1.25	2.15	0.90
128	4.21	2.11	3.75	1.43	3.65	1.22
512	4.88	2.27	4.63	1.61	4.55	1.36
1024	5.05	2.31	4.87	1.66	4.80	1.40
2048	5.15	2.34	5.06	1.70	4.89	1.41

 μ_∞ Values (found)

V	0°	15°	25°	35°
2048	220.00	297.30	347.91	396.83

 μ_∞ Values (calculated from sodium salt)

V	0°	15°	25°	35°
2048	220.20	297.31	347.97	396.90

Table LXI.—Percentage Dissociation

V	0°	15°	25°	35°
32	75.68	71.34	68.39	65.49
128	90.55	88.21	85.96	84.74
512	97.70	96.93	95.90	95.47
1024	99.35	98.67	98.50	98.49
2048	100.00	100.00	100.00	100.00

1,3,5-Dinitrobenzoic Acid, C₆H₃(NO₂)₂COOH

The acid was precipitated from alcoholic solution by means of water. It melted at 205°.

Although the conductivity and dissociation of this acid are fairly high, there is a wide difference between the values for this acid and the corresponding values for the preceding acid. The conductivity and dissociation of the 1,2,4-acid reach a maximum at N/2048, whereas the 1,3,5-acid is only 78.7 per cent. dissociated at the same dilution.

It should be noted that the μ_{∞} values of the two acids, however, are practically identical. Moreover, in the case of the 1,2,4-acid, the maximum value of conductivity as measured directly agrees with that obtained from the sodium salt. The fact that the values of the sodium salt prepared by titration agree with those of the salt made up by weight has already been mentioned.

Table LXII.—Molecular Conductivity

V	0°	15°	25°	35°
512	122.28	171.4	203.6	233.5
1024	147.86	205.4	244.0	280.0
2048	167.63	231.9	273.5	313.0

Table LXIII.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	3.23	2.64	3.22	1.88	2.99	1.47
1024	3.84	2.60	3.87	1.88	3.59	1.47
2048	4.23	2.52	4.16	1.79	3.95	1.44

Table LXIV.—Percentage Dissociation

V	0°	12°	25°	35°
512	55.52	57.62	58.60	58.83
1024	67.14	69.06	70.23	70.54
2048	76.12	77.96	78.72	78.86

Table LXV.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	13.5	15.3	16.2	16.4
1024	13.4	15.1	16.2	16.5
2048	11.9	13.5	14.2	14.4

o-Chlorbenzoic Acid, $C_6H_4Cl.COOH$

The acid was purified by the precipitation of the alcoholic solution with water, and was dried in an air bath at 105°. The slightest friction causes the dry acid to become highly charged electrically, so that special precautions must be taken not to agitate it, any more than necessary, before weighing, and it was found best to use a closed bottle for this purpose.

The values found by Ostwald¹ for 25° are given below because they differ quite appreciably from our own at the higher dilutions:

Ostwald					
V	μ_v 25°	α 25°	V	μ_v 25°	α 25°
128	119.4	33.5	512	197.0	55.3
256	156.1	43.8	1024	238.7	67.1

$$K = 13.2$$

After noticing this disagreement, a second determination was made with a N/512 solution of the acid and a N/2048 solution of the salt at 25°, in order to see whether there had not been some error in making up the first solutions. The following is the result of the second measurement as compared with the first:

	First determination 25°	Second determination 25°
Acid..... 512	194.05	193.82
Sodium salt.. 2048	75.47	75.56

The difference in the two determinations of conductivity, both for the acid and the sodium salt, is less than two-tenths of one per cent.

The value of K as found by ourselves ($K = 13.6$) is fairly close to that found by Ostwald.

As compared with the nitro substitution product ($K = 4.14$) it is seen from the tables that the chlorine substitution product ($K = 13.6$) has much the larger values both of conductivity

¹ Z. physik. Chem., **3**, 255 (1889).

and dissociation, and the latter has a constant, at 25°, over four times as large as the former.

o-Chlorbenzoic Acid

Table LXVI.—Molecular Conductivity

V	0°	15°	25°	35°
128	85.20	107.08	118.91	128.39
256	109.00	138.40	154.12	167.12
512	134.81	172.70	194.05	211.86
1024	158.72	205.64	232.91	256.43
2048	178.00	233.29	266.52	296.94

Table LXVII.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.46	1.71	1.18	1.11	0.95	0.80
256	1.96	1.80	1.57	1.14	1.30	0.84
512	2.52	1.87	2.13	1.24	1.78	0.92
1024	3.13	1.97	2.73	1.33	2.35	1.01
2048	3.68	2.07	3.32	1.42	3.04	1.14

Table LXVIII.—Percentage Dissociation

V	0°	15°	25°	35°
128	38.66	35.94	34.12	32.32
256	49.45	46.45	44.22	42.06
512	61.16	57.96	55.67	53.33
1024	72.00	69.01	66.82	64.54
2048	80.76	78.29	76.46	74.74

Table LXIX.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	19.0	15.8	13.8	12.1
256	18.9	15.7	13.7	11.9
512	18.8	15.6	13.7	11.9
1024	18.1	15.0	13.1	11.5
2048	16.6	13.8	12.1	10.8

1,2,4-Dihydroxybenzoic Acid, $\text{C}_6\text{H}_3(\text{OH})_2\text{COOH}$

The acid was precipitated from alcohol by water. It decomposed at 213°.

Table LXX.—Molecular Conductivity

V	0°	15°	25°	35°
128	44.74	65.11	79.27	92.14
512	80.73	116.40	140.15	162.02
1024	103.30	147.77	177.20	203.58
2048	127.65	180.58	215.81	248.28

Table LXXI.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.36	2.04	1.42	2.17	1.28	1.62
512	2.38	2.95	2.38	2.04	2.19	1.56
1024	2.97	2.87	2.94	1.99	2.64	1.46
2048	3.53	2.77	3.52	1.92	3.25	1.50

Table LXXII.—Percentage Dissociation

V	0°	15°	25°	35°
128	20.16	21.71	22.70	23.10
512	36.37	38.82	40.12	40.62
1024	46.54	49.28	50.73	51.04
2048	57.51	60.22	61.79	62.24

Table LXXIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	3.98	4.62	5.21	5.42
512	4.06	4.81	5.25	5.43
1024	3.94	4.66	5.08	5.12
2048	3.80	4.45	4.88	5.01

1,2,5-Dihydroxybenzoic Acid, C₆H₃(OH)₂COOH

The acid was purified like the 1,2,4 compound. It melted at 200°.

It was found to decompose rapidly in the presence of the platinum electrodes, giving a yellow solution; therefore, measurements had to be made as quickly as possible, and a fresh solution had to be introduced into the cells after each reading. This decomposition accounts, no doubt, for the disagreement with Ostwald's values.

Like the two dinitrobenzoic acids given above, these two acids, 1,2,4- and 1,2,5-dihydroxybenzoic acids, have μ_{∞} values which agree, though the conductivities and dissociations of the two are quite different. The constants of the 1,2,5-acid ($K_{25^{\circ}} = 12.8$) are more than twice as great as those of the 1,2,4-acid ($K_{25^{\circ}} = 5.11$). Ostwald¹ has given a very complete discussion of the relation of the various hydroxybenzoic acids to each other, so that reference only need be made to them here.

¹ Z. physik. Chem., **3**, 247–51 (1889).

Table LXXIV.—Molecular Conductivity

V	0°	15°	25°	35°
128	66.18	95.50	113.96	131.22
512	114.49	163.00	191.90	219.43
1024	141.50	200.68	234.70	267.72
2048	184.36	252.38	290.83	328.42

Table LXXV.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	1.95	2.94	1.85	1.93	1.73	1.52
512	3.23	2.83	2.89	1.77	2.75	1.43
1024	3.95	2.79	3.40	1.70	3.30	1.41
2048	4.54	2.46	3.86	1.52	3.76	1.29

Table LXXVI.—Percentage Dissociation

V	0°	15°	25°	35°
128	29.85	31.87	32.49	32.83
512	51.63	54.39	54.71	54.89
1024	63.82	66.97	66.91	66.98
2048	83.15	84.22	82.92	82.17

Table LXXVII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
128	9.9	11.7	12.2	12.5
512	10.8	12.7	12.9	13.0
1024	10.6	13.3	13.2	13.3
2048	23.9	22.0	19.7	18.5

p-Sulphamidobenzoic Acid, $\text{H}_2\text{NO}_2\text{S.C}_6\text{H}_4\text{COOH}$

The acid was purified by crystallization. When dry it decomposes at 280° .

We notice here the difference between the amino acids, such as metanilic, sulphanilic, and *o*- and *p*-aminobenzoic acids¹ and the acid amides containing another acid radical. Whereas the temperature coefficients increase with rise in temperature and are very large in the former case, in the latter the temperature coefficients are perfectly normal. The amino group neutralizes the sulpho group but has no effect, practically, on the carboxyl group.

¹ Am. Chem. J., **44**, 189 (1910).

The strength of *p*-sulphamidobenzoic acid as compared with that of the amino acids is seen in the following list of constants:

<i>o</i> -Aminobenzoic acid	$K = 0.0671$
<i>p</i> -Aminobenzoic acid	$K = 0.0714$
Metanilic acid	$K = 1.99$
<i>p</i> -Sulphamidobenzoic acid	$K = 2.96$
Sulphanilic acid	$K = 6.55$

Table LXXVIII.—Molecular Conductivity

V	0°	15°	25°	35°
512	67.79	96.00	113.02	128.03
1024	90.60	124.82	146.94	167.17
2048	114.55	157.37	185.11	210.05

Table LXXIX.—Temperature Coefficients

V	0°–15°		25°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	1.88	2.77	1.70	1.77	1.50	1.17
1024	2.28	2.52	2.21	1.77	2.02	1.21
2048	2.85	2.49	2.77	1.76	2.49	1.19

μ_{∞} Values

V	0°	15°	25°	35°
2048	221.70	299.29	349.77	398.0

Table LXXX.—Percentage Dissociation

V	0°	15°	25°	35°
512	30.59	32.06	32.31	32.17
1024	40.88	41.69	42.01	42.01
2048	51.68	52.56	52.92	52.79

Table LXXXI.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	2.63	2.96	3.01	2.98
1024	2.76	2.91	2.97	2.97
2048	2.70	2.84	2.91	2.88

Benzenesulphonic Acid, $C_6H_5.SO_3H$

The acid was recrystallized from water, but not dried, since the acid is very hygroscopic. It was standardized in the same way as trichloroacetic acid.

It should be noted that the temperature coefficients of strong acids like benzenesulphonic, trichloroacetic acids, etc., are much larger than those of the weaker acids, and the increase

in the temperature coefficients with dilution, as well as the decrease with temperature, is very much less rapid.

Table LXXXII.—Molecular Conductivity

V	0°	15°	25°	35°
8	204.57	275.38	321.07	366.1
32	210.23	281.69	326.55	370.1
128	222.14	300.43	350.47	399.3
512	226.92	305.81	356.38	407.0
1024	228.00	308.97	359.03	410.0
2048	226.83	305.71	354.22	407.0

Table LXXXIII.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.72	2.31	4.57	1.66	4.50	1.40
32	4.76	2.27	4.49	1.59	4.35	1.33
128	5.22	2.35	5.00	1.67	4.93	1.41
512	5.26	2.32	5.05	1.65	5.06	1.42
1024	5.40	2.37	5.01	1.62	5.13	1.43
2048	5.26	2.32	4.85	1.59	5.29	1.49

μ_{∞} Values

V	0°	15°	25°	35°
2048	228.00	308.97	359.03	410.3

Table LXXXIV.—Percentage Dissociation

V	0°	15°	25°	35°
8	89.72	89.13	89.43	89.23
32	92.21	91.17	90.95	90.20
128	97.43	97.24	97.62	97.44
512	99.53	98.98	99.26	99.20
1024	100.00	100.00	100.00	100.00

p-Toluenesulphonic Acid, $\text{H}_3\text{C.C}_6\text{H}_4.\text{SO}_3\text{H}$

This acid is similar to benzenesulphonic acid. It has a somewhat lower conductivity, although its percentage dissociation is a little greater (the increase to a maximum, in the case of benzenesulphonic acid, is at a slower rate).

Table LXXXV.—Molecular Conductivity

V	0°	12°	25°	35°
32	203.0	258.5	317.3	361.4
128	208.4	267.0	328.2	374.2
512	210.0	269.0	331.7	376.4
1024	210.6	269.7	332.7	379.3
2048	206.7	266.4	327.7	372.3

Table LXXXVI.—Temperature Coefficients

V	0°–12°		12°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	4.62	2.28	4.52	1.75	4.41	1.39
128	4.88	2.34	4.76	1.76	4.60	1.40
512	4.92	2.35	4.82	1.79	4.66	1.41
1024	4.93	2.34	4.84	1.80	4.67	1.40
2048	4.97	2.40	4.76	1.79	4.46	1.36

 μ_{∞} Values

V	0°	12°	25°	35°
2048	210.6	269.7	332.7	379.3

Table LXXXVII.—Percentage Dissociation

V	0°	12°	25°	35°
32	96.40	95.85	95.39	95.30
128	98.97	99.00	98.68	98.68
512	99.72	99.74	99.70	99.26
1024	100.00	100.00	100.00	100.00

m-Nitrobenzenesulphonic Acid, $\text{O}_2\text{N.C}_6\text{H}_4.\text{SO}_3\text{H}$

This acid is similar to the two preceding acids, except that it is not quite so hygroscopic and could be more easily handled. Its conductivity is a little less than that of benzenesulphonic acid, but its dissociation is greater.

Table LXXXVIII.—Molecular Conductivity

V	0°	16°	25°	35°
32	195.9	262.9	307.1	350.0
128	200.5	269.1	313.8	357.2
512	202.0	272.9	320.4	367.2
1024	204.3	275.5	323.5	369.4
2048	204.3	274.6	321.5	368.3

Table LXXXIX.—Temperature Coefficients

V	0°–16°		16°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	4.47	2.28	4.42	1.68	4.29	1.40
128	4.57	2.28	4.47	1.66	4.34	1.38
512	4.73	2.34	4.75	1.74	4.68	1.46
1024	4.73	2.31	4.20	1.74	4.59	1.42
2048	4.69	2.30	4.69	1.71	4.68	1.45

 μ_{∞} Values

V	0°	16°	25°	35°
1024	204.5	275.5	223.5	369.4

Table XC.—Percentage Dissociation

V	0°	16°	25°	35°
32	95.60	95.43	94.92	94.75
128	97.84	97.68	97.00	96.69
512	98.58	99.09	99.04	99.40
1024	100.00	100.00	100.00	100.00

1,2,4-Nitrotoluenesulphonic Acid, C₆H₃.CH₃.NO₂.SO₃H

The acid is very much like the preceding. It is not quite as strong as nitrobenzenesulphonic acid, as would be expected.

Table XCI.—Molecular Conductivity

V	0°	15°	25°	35°
8	176.9	240.9	275.6	312.6
32	193.0	264.1	303.6	344.2
128	198.4	272.0	312.4	354.7
512	199.9	274.3	315.6	358.6
1024	200.5	276.5	318.4	361.9
2048	199.7	274.5	314.8	357.6

Table XCII.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units.	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.00	2.26	3.86	1.60	3.70	1.34
32	4.44	2.30	4.31	1.63	4.06	1.34
128	4.60	2.32	4.49	1.65	4.23	1.35
512	4.65	2.33	4.59	1.67	4.30	1.36
1024	4.74	2.37	4.67	1.69	4.35	1.37
2048	4.67	2.34	4.48	1.63	4.28	1.36

 μ_{∞} Values

V	0°	15°	25°	35°
1024	200.5	276.5	318.4	361.9

Table XCIII.—Percentage Dissociation

V	0°	15°	25°	35°
8	88.22	87.12	86.94	86.38
32	96.27	95.52	95.35	95.13
128	98.97	98.37	98.13	98.02
512	99.62	99.22	99.10	99.08
1024	100.00	100.00	100.00	100.00

4,5-Dichlorophthalic Acid, C₆H₂Cl₂(COOH)₂

The acid was purified by crystallization from water.

The conductivity of this acid as compared with that of

o-phthalic acid¹ is about 1.5 times as great. This acid evidently dissociates as a dibasic acid, that is, both hydrogens are dissociated, since its conductivity is too great for that of a monobasic acid. One can see from this that it is not possible to find the μ_{∞} values of the acid by the graphic method, because this method is applicable only to acids dissociating as monobasic acids.

Nor was it possible to obtain μ_{∞} for the sodium salt with the cells we were using. Further work will be carried out later with cells of the cylindrical type on this and the two following acids in order to obtain their μ_{∞} values.

Table XCIV.—Molecular Conductivity

V	0°	15°	25°	35°
128	194.24	353.00	286.82	318.34
512	238.55	314.66	359.02	398.42
1024	263.80	348.53	397.13	440.78
2048	288.09	378.49	436.03	487.47

Table XCV.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
128	3.91	2.01	1.38	1.33	3.15	1.10
512	5.07	2.13	4.44	1.41	3.94	1.10
1024	5.65	2.14	4.86	1.39	4.37	1.10
2048	6.03	2.09	5.75	1.52	5.14	1.18

Tetrachlorophthalic Acid, C₆Cl₄(COOH)₂

This acid was an exceptionally pure one obtained from Professor W. R. Orndorff and T. G. Delbridge, of Cornell, who had carried out an investigation on its composition and method of purification.²

Tetrachlorophthalic acid is quite similar, in general, to dichlorophthalic acid, though its conductivity is much greater.

Table XCVI.—Molecular Conductivity

V	0°	15°	25°	35°
512	296.8	386.5	441.3	492.7
1024	328.6	432.7	495.9	555.2
2048	356.0	469.2	539.8	605.0

¹ Am. Chem. J., **44**, 187 (1910).

² *Ibid.*, **41**, 393 (1909).

Table XCVII.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	5.98	2.02	5.48	1.42	5.14	1.17
1024	6.94	2.11	6.32	1.46	5.93	1.20
2048	7.55	2.12	7.06	1.50	6.52	1.21

Meconic Acid, $(\text{HO})\text{C}_5\text{HO}_2(\text{COOH})_2 + 3\text{H}_2\text{O}$

The acid was purified by precipitation from alcohol with water.

Table XCVIII.—Molecular Conductivity

V	0°	15°	25°	35°
32	...	358.6	412.8	146.4
128	347.8	463.2	536.4	598.9
512	412.8	553.6	645.4	729.5
1024	435.9	586.8	686.2	778.0
2048	442.1	597.3	700.1	802.7

Table XCIX.—Temperature Coefficients

V	0°-15°		15°-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	...	..	5.42	1.58	4.86	1.18
128	7.69	2.21	7.32	1.44	6.25	1.17
512	9.39	2.27	9.18	1.65	8.41	1.33
1024	10.06	2.36	9.94	1.69	9.18	1.34
2048	10.35	2.34	10.28	1.72	10.26	1.47

It is the strongest of all the acids with which we worked. It has the highest percentage temperature coefficients and a conductivity approaching closely to that of sulphuric acid, although it does not give a maximum conductivity.

V	<i>Sulphuric Acid</i> Jones and West ¹		<i>Meconic Acid</i> From Table XCVIII	
	μ_{25} 25°	Cond. units	μ_{25} 25°	Cond. units
32	491.4	4.22	412.8	4.86
128	589.4	5.68	536.4	6.25
512	675.2	7.78	645.4	8.41
1024	...	...	686.2	9.18
2048	709.9	10.45	700.1	10.26

¹ Am. Chem. J., 34, 414 (1905).

Camphoric Acid, C₁₀H₁₆O₄

The acid was purified like meconic acid.

It is stronger than the acids of the aliphatic series, but is much weaker than those of the aromatic series. It dissociates, as can be seen from Table CII, like a weak monobasic acid, though it titrates as a dibasic acid.

Table C.—Molecular Conductivity

V	0°	12°	25°	35°
512	24.94	33.05	38.17	42.57
1024	34.05	45.27	52.12	57.99
2048	45.10	59.54	68.15	76.12

Table CI.—Temperature Coefficients

V	0°–12°		12°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
512	0.541	2.17	0.512	1.55	0.440	1.15
1024	0.748	2.20	0.685	1.57	0.587	1.13
2048	0.963	2.14	0.861	1.46	0.797	1.17

 μ_{∞} Values (from curve)

	0°	12°	25°	35°
	218.3	279.8	344.5	392.5
$K_{15} = [218.3 + (5.2 \times 12) - (0.00609 \times 144)] = 279.8$				

Table CII.—Percentage Dissociation

V	0°	15°	25°	35°
512	11.43	11.81	11.08	10.85
1024	15.60	16.18	15.13	14.78
2048	20.66	21.28	19.78	19.40

Table CIII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
512	0.288	0.309	0.270	0.259
1024	0.282	0.305	0.264	0.250
2048	0.263	0.289	0.238	0.228

Uric Acid, C₅H₄N₄O₃

The acid was crystallized from water, a small quantity at a time.

Its slight solubility made it impossible to determine its conductivity at any dilution lower than N/2048. It is seen

to be a *very* weak acid, its constant at 25° ($K = 0.0151$) being only about one-fifth that of *p*-aminobenzoic acid ($K = 0.0714$).

Table CIV.—Molecular Conductivity

V	0°	15°	25°	35°
2048	8.34	14.85	18.92	22.77

Table CV.—Temperature Coefficients

V	0°–15°		15°–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2048	0.434	5.20	0.404	2.72	0.385	2.03

μ_{∞} Values (determined graphically)

V	0°	15°	25°	35°
2048	221.0	298.8	350.0	399.9

$K_{15} = [221.0 + (5.28 \times 15) - (0.00486 \times 225)] = 299.1$

Table CVI.—Percentage Dissociation

V	0°	15°	25°	35°
2048	3.77	4.97	5.41	5.71

Table CVII.—Dissociation Constants $\times 10^4$

V	0°	15°	25°	35°
2048	0.0072	0.0127	0.0151	0.0169



The acid was purified by recrystallization from water.

Its conductivity is so small that it required resistances of over 10,000 ohms to be thrown into the circuit in order to obtain the minimum on the bridge at 35° and measurements at temperatures below this were so inaccurate that they are not given.

Constants could not be obtained with the use of the Ostwald dilution law.

Table CVIII.—Molecular Conductivity

V	35°	V	35°
128	1.46	1024	3.52
512	2.78	2048	4.67

Table CIX.—Percentage Dissociation

V	35°	V	35°
128	0.360	1024	0.869
512	0.686	2048	1.15

The following acids were tested but were found to be either too insoluble or they decomposed too rapidly:

Thioacetic (decomposed)
 Tribromacetic (decomposed)
 Phenylbromacetic (decomposed)
 Sebacic (insoluble)
p-Brombenzoic (insoluble)
p-Chlorbenzoic (insoluble)
 Isophthalic (insoluble)
 Brompalmitic (insoluble)
 Benzenesulphinic (insoluble)

α -Naphthylaminesulphonic acid and gluconic acid were both tested, but it was found that the solutions had not been standardized properly so they were, for the time being, discarded.

DISCUSSION OF RESULTS

The temperature coefficients of conductivity, expressed in conductivity units, for all the above acids show an increase with dilution of the solution and a decrease with rise in temperature. The rate of increase and decrease is, of course, larger for some acids than for others. The general rule seems to be that the stronger the acid, the less rapid is both the increase with dilution and the decrease with rise in temperature. The very fact that the dissociation of strong acids is so large for all dilutions readily accounts for the small change in the coefficients with dilution.

We know that the temperature coefficients of conductivity for even strong *mineral* acids decrease, to a small extent, with rise in temperature;¹ and also that most of the strong mineral acids are more or less hydrated when in aqueous solution. It is evident that if an acid were not hydrated or only very slightly hydrated (as is the case with most of the weak organic acids), then the decrease in temperature coefficients with rise in temperature would be more rapid, since the complex, hydrated ions could not lose much water, and in consequence, the conductivity could not thus be greatly increased. In order to make this clearer, we have collected in Table CX the values of the temperature coefficients of conductivity for a number

¹ Am. Chem. J., **34**, 418 (1905).

of weak and practically nonhydrated acids, expressed in conductivity units, for the dilution $N/1024$ between 0° and 35° .

Table CX.

Acid.	K_0	$0^\circ-15^\circ$	$15^\circ-25^\circ$	$25^\circ-35^\circ$	Decrease Per cent.
Uric.....	0.0072	0.43	0.40	0.39	11.6
Caprylic.....	0.125	0.56	0.51	0.45	19.6
Propionic ¹	0.133	0.61	0.59	0.51	16.4
Acetic ¹	0.175	0.72	0.69	0.62	13.9
Levulinic.....	0.220	0.81	0.79	0.71	12.4
Camphoric.....	0.285	0.75	0.69	0.59	21.3

In Table CXI are found the similar values for some of the hydrated acids. There are, in addition to the four strong acids in this table, also two weaker acids—racemic and citric acids—and these show the same decrease in the coefficients as the strong acids.

Table CXI

Acid	Water of cryst. H_2O	$0^\circ-15^\circ$	$15^\circ-25^\circ$	$25^\circ-35^\circ$	Decrease Per cent.
Meconic.....	3	10.06	9.94	9.18	8.8
Benzenesulphonic.....	1	5.26	5.05	5.06	3.8
<i>p</i> -Toluenesulphonic.....	4	4.92	4.84	4.67	5.3
1,2,4-Nitrotoluenesulphonic	2.5	4.74	4.67	4.35	8.2
Racemic, ² $K_0 = 9.1$	1	3.76	3.56	3.43	8.0
Citric, ² $K_0 = 6.85$	1	3.64	3.59	3.38	7.1

This indicates that the strength of the acid has very little to do with the gradual decrease in temperature coefficients, but that this decrease is caused by hydration; and the above relation applies to the strong acids only because they are the acids which are most hydrated.

Another interesting point that should be brought out in connection with the temperature coefficients expressed in conductivity units is that the strong acids have the much larger coefficients. This is shown by the following table, which contains the conductivity units of the $N/2048$ solutions of a number of acids between 0° and 15° , the acids being arranged according to their strength:

¹ White and Jones: Am. Chem. J., **44**, 159 (1910).

² *Loc. cit.*

Table CXII

Acid	Cond. units 0°-15°	K
Uric.....	0.434	0.0072
Isovaleric.....	0.699	0.125
Levulinic.....	1.13	0.220
β -Iodopropionic.....	1.76	0.977
<i>p</i> -Sulphamidobenzoic.....	2.95	2.70
1,2,4-Dihydroxybenzoic...	3.53	3.95
α -Bromopropionic.....	3.70	12.4
α -Brombutyric.....	3.82	14.98
Cyanacetic.....	4.70	38.7
<i>p</i> -Toluenesulphonic.....	4.97	(completely dissociated)
Meconic.....	10.35	

White and Jones found that the percentage temperature coefficients for very nearly all the acids with which they worked showed a slight decrease with increasing dilution, and a much more marked decrease with rise in temperature. We find that the latter decrease is shown by all the acids with which we worked, but there are a number of exceptions to the decrease in temperature coefficients with dilution, probably due to hydrolysis.

All the percentage temperature coefficients of all the acids except uric acid are small, and of the same order of magnitude—not greater than 2.8 per cent. and not less than 2.0 per cent. from 0°-15°—and decrease to 1.7-1.0 per cent. from 25°-35°. That this decrease¹ is regular and of the same order of magnitude throughout would seem to indicate that some constant factor, such as the viscosity of the medium, plays the most important rôle here, and that the viscosity decreases with increasing dilution and rising temperature at the same diminishing rate. That the latter is true is seen from the following data, showing the viscosity of thiodiglycolic acid in aqueous solution:

Table CXIII

	Viscosity at 15°	Viscosity at 25°	Viscosity at 35°
Water ²	0.01134	0.00891	0.00720
N/2048 solution.....	...	0.00896	...
N/8 solution.....	0.01188	0.00927	0.00750

¹ For a full discussion of the decrease in percentage temperature coefficients see Jones and West: *Am. Chem. J.*, **34**, 418 (1905).

² Thorpe and Rogers: *Phil. Trans.*, **185**, 307 (1894); **189**, 71 (1897).

That the conductivity of organic acids is a parabolic function of the temperature was brought out by Schaller and other earlier workers, and by the work of White and Jones, as we have already had occasion to mention in the introduction to this paper. White and Jones plotted several curves, using conductivities as ordinates and temperatures as abscissae, and calculated the conductivity of a number of acids by means of the formula

$$\mu_t = \mu_0 + at - bt^2$$

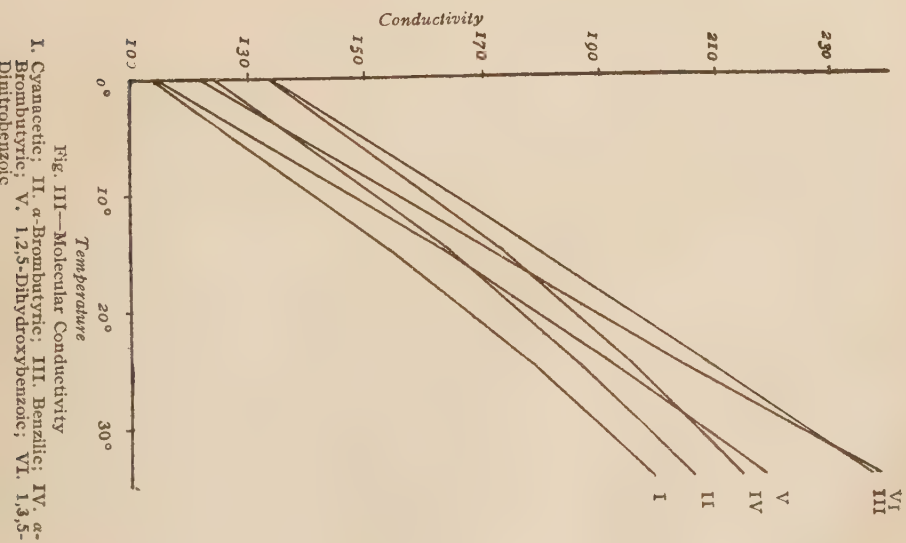
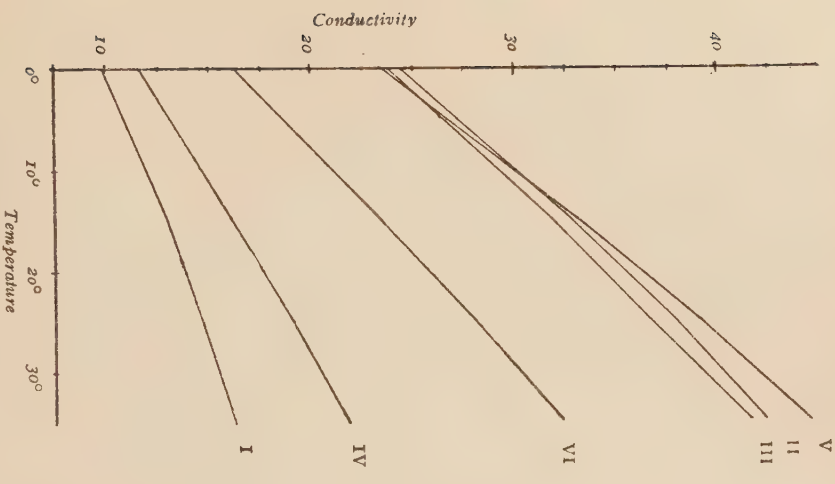
and found this law to hold in every case.

The curves in Figs. II-V and the values given in Table CXIV are also all in perfect accord with the law, which seems to hold whether the acid is strong or weak monobasic, dibasic or tribasic. The observed and calculated values in the last two columns of the table are seen to agree very closely.

Table CXIV

	μ_0	a	b	t	Obs.	Calc.
Trichloracetic.....	221.7	5.24	0.0127	15°	297.6	297.5
α -Brompropionic...	124.7	2.84	0.0141	15°	164.1	164.1
β -Iodpropionic.....	23.79	0.526	0.00040	15°	31.86	31.59
Levulinic.....	11.57	0.318	0.00070	15°	16.13	16.18
α -Brombutyric.....	133.7	2.81	0.0140	15°	173.2	172.7
Hydroxyisobutyric	23.50	0.684	0.00229	15°	33.04	33.24
Isovaleric.....	9.85	0.224	0.00122	15°	12.92	12.94
Thiodiglycolic.....	93.31	2.37	0.00606	15°	127.47	127.50
Tricarballic.....	31.82	0.927	0.00162	15°	45.13	45.36
1,3,5-Dinitrobenzoic	122.3	3.43	0.00750	15°	171.4	172.0
1,2,5-Dihydroxy- benzoic.....	114.5	3.35	0.00983	15°	163.0	162.5
<i>p</i> -Sulphamidobenzoic	90.60	2.41	0.00660	15°	124.8	125.2
Benzenesulphonic..	222.1	5.27	0.00563	15°	300.4	300.0
<i>p</i> -Toluenesulphonic	208.4	4.93	0.00549	12°	267.0	266.8
1,2,4-Nitrotoluene- sulphonic.....	198.4	4.79	0.00945	16°	272.0	272.6
Dichlorphthalic...	194.2	4.10	0.01576	15°	253.0	252.2

The dissociation of a large number of the acids decreases steadily with rise in temperature. In other cases the percentage dissociation apparently reaches a maximum at some temperature between 15° and 35°, usually around 25°. There are still others whose percentage dissociation increases all



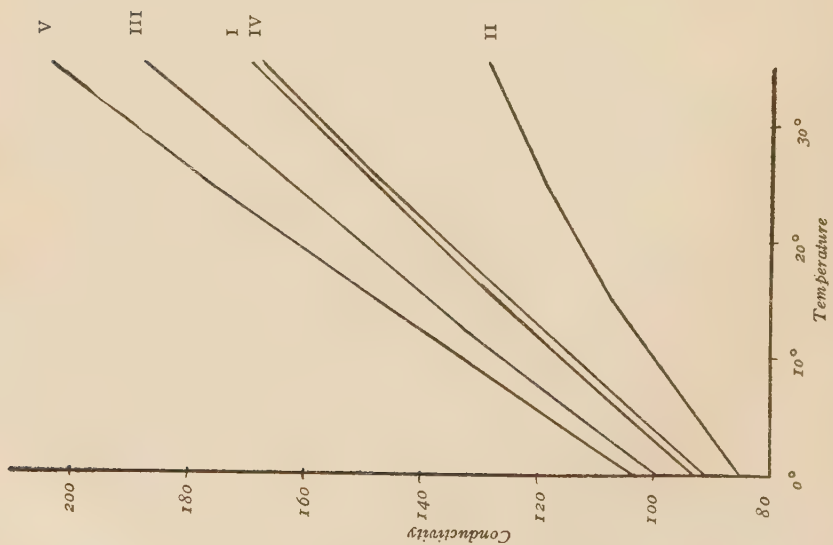


Fig. IV—Molecular Conductivity
 I. Thiodiglycolic; II. α -Bromopropionic; III. Benzilic; IV. α -Bromobutyric; V. 1,2,5-Dihydroxybenzoic; VI. 1,3,5-Dinitrobenzoic

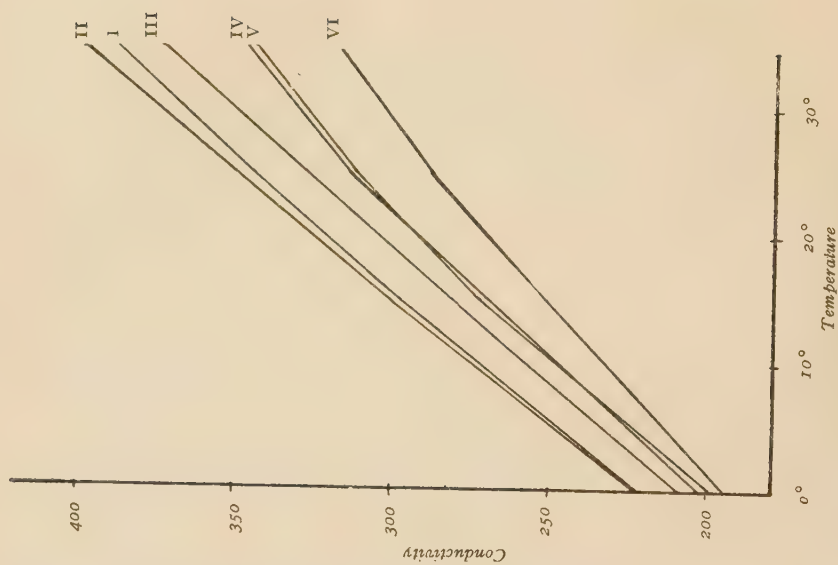


Fig. V—Molecular Conductivity
 I. Trichloroacetic; II. Benzenesulphonic; III. *p*-Toluenesulphonic; IV. *m*-Nitrobenzenesulphonic; V. 1,2,4-Nitrophenesulphonic; VI. Dichlorophthalic

the way up to 35°, though at a diminishing rate. The latter phenomenon is not unusual, Euler,¹ Schaller,² and White and Jones,³ all having observed the same increase in dissociation for more than a dozen acids.

No adequate explanation, however, has been offered, and the problem is a complex one, since there are several factors which can influence the dissociation. Decrease in the association and in the dielectric constant of the solvent with rise in temperature are two well-known causes for the decrease in the dissociating power; and rise in temperature alone, which produces a greater instability in the molecules and a larger ionic mobility, would tend to cause an *increase* in the dissociation. The nature of the dissolved substance itself very likely plays some part, and when all these factors are taken into account, it seems practically impossible to predict beforehand what the result would be.

The following table contains the dissociation constants for all except the strong acids, calculated by means of Ostwald's law:

Table CXV.—Dissociation Constants $\times 10^4$

Acid	0°	15°	25°	35°
Cyanacetic.....	38.7	37.5	36.3	34.8
Benzilic.....	9.25	9.15(12°)	9.20	8.93
α -Brompropionic.....	12.4	12.4	10.4	9.2
β -Iodopropionic.....	0.977	0.945	0.917	0.910
Levulinic.....	0.220	0.230	0.243	0.246
α -Brombutyric.....	14.98	16.1	12.7	11.5
Hydroxyisobutyric....	0.96	1.04	1.06	1.07
Isovaleric.....	0.167	0.153	0.149	0.141
Caprylic.....	0.125	0.126	0.129	0.123
<i>l</i> -Tartaric.....	9.45	10.1	10.7	10.7
Thiodiglycolic.....	6.38	6.50	6.51	6.36
Tricarballic.....	1.92	2.14	2.24	2.30
<i>p</i> -Nitrobenzoic.....	3.62	3.99(12°)	4.14	4.14
1,3,5-Dinitrobenzoic...	13.4	15.2	16.2	16.4
<i>o</i> -Chlorbenzoic.....	13.7	15.5	13.6	11.9
1,2,4-Dihydroxybenzoic	3.95	4.64	5.11	5.25
1,2,5-Dihydroxybenzoic	10.4	12.6	12.8	12.9
<i>p</i> -Sulphamidobenzoic	2.70	2.90	2.96	2.94
Camphoric.....	0.285	0.307(12°)	0.267	0.254
Uric.....	0.0072	0.0127	0.0151	0.0169

¹ Z. physik. Chem., **21**, 247 (1896).

² *Ibid.*, **25**, 497 (1898).

³ Am. Chem. J., **44**, 196 (1910).

A more general, though empirical, equation for calculating the constants was suggested by Storch,¹ and employed by Bancroft,² Noyes,³ and others, viz.,

$$K = C_i^n / C_s$$

in which $C_i = \frac{\alpha}{V}$ denotes the volume concentration of the dissociated portion, and $C_s = \frac{1-\alpha}{V}$, the volume concentration of the undissociated part; K and n are both functions of the electrolyte. By using C_i as values along the ordinates and C_s as values along the abscissae, a curve can be plotted from which it is possible to obtain n . The values for n found by previous workers, for a large number of salts and acids, vary from 1.36 to 1.55.

We have attempted by means of this method to obtain constants for the strong acids, but the equation did not seem to be applicable to this case.

Further work on the organic acids, and also on the organic bases, both in aqueous and in nonaqueous solutions, and through a wider range of temperature, is being carried out in this laboratory.

SUMMARY

Several conclusions reached by White and Jones have been confirmed by the present work and are repeated here in quotation marks.

1. The temperature coefficients of conductivity, expressed in conductivity units, increase rapidly with dilution, and decrease rapidly with rise in temperature for weak organic acids—when not hydrated. When the acids are hydrated, the temperature coefficients of conductivity are larger, and their increase with dilution and decrease with rise in temperature both take place at a slower rate.

2. Organic acids with the largest constants also have the largest temperature coefficients of conductivity expressed in conductivity units.

¹ Z. physik. Chem., **19**, 13 (1896).

² *Ibid.*, **31**, 188 (1889).

³ J. Am. Chem. Soc., **26**, 137 (1906); **30**, 333 (1908).

3. "The percentage temperature coefficients of conductivity of the organic acids are generally small and of the same order of magnitude, and decrease with rise in temperature and with increase in dilution."

4. "The conductivity of most of the organic acids is a parabolic function of the temperature, as proved by comparing observed values with those calculated from interpolation formulae."

5. "There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between 25° and 35° , while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from 0° ."

6. The strong organic acids do not obey the Ostwald dilution law, and, therefore, dissociation constants cannot be obtained for them in the ordinary way.

7. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anion, and μ_{∞} values for dibasic acids may be found by means of this principle.

8. Most dibasic organic acids dissociate like monobasic acids.

9. "Isomeric acids do not behave similarly as regards change in their dissociation."

10. "The migration velocities of isomeric ions are identical."

11. "The behavior of the organic acids with respect to the change in their dissociation with the temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants, or at least the influence of some other unknown force is suggested."

JOHNS HOPKINS UNIVERSITY,
May, 1911

BIOGRAPHICAL.

Eugene Pinckney Wightman was born in Baltimore, Md., on December 24, 1888. He received his early education in the public schools of Baltimore. In 1902 he went to live in Ashland, Va., where he attended the Ashland High School for three years. In September, 1905, he began his collegiate training at Randolph-Macon College at Ashland, and there he was in attendance one session. For the next two years he studied at Richmond College, Richmond, Va., where in June, 1908, he received the degree of Bachelor of Science. The following October he entered the Johns Hopkins University, as a graduate student in Chemistry, receiving a Hopkins Scholarship. This was continued during the two succeeding years.

JOHNS HOPKINS UNIVERSITY,
June, 1911.

